

Assessment of Costs and Benefits of Flexible and Alternative Fuel Use in the U.S. Transportation Sector

Technical Report Seven: Environmental, Health, and Safety Concerns

October 1991

**United States Department of Energy
Office of Policy, Planning and Analysis
Washington, DC 20585**

This report is based on a study that Argonne National Laboratory prepared for the Department of Energy's Office of Environmental Analysis in the Office of Policy, Planning and Analysis.

CONTENTS

INTRODUCTION AND EXECUTIVE SUMMARY	vi
METHANOL VEHICLES	1
Introduction	1
Emissions and Air Quality	1
Emissions from Spark-Ignition Engines	1
Factors Affecting Emissions	1
Hydrocarbons	3
Aldehydes	4
Carbon Monoxide	4
Oxides of Nitrogen	4
Methyl Nitrite	4
Emissions From Compression-Ignition Engines	4
Methanol-Diesel Fuel Emulsions	5
Ignition-Improving Additives	6
Spark-Assisted Ignition	6
Glow-Plug and Surface-Ignition	6
In-Use Performance	6
Unresolved Technical Issues Affecting Vehicle Emissions	7
Engine Life and Maintenance	7
Changes in Components and Control Systems	7
Durability of Emission-Control and Fuel Systems	7
Cold Starting	7
Hot Starting	8
Fuel Distribution System Emissions	8
Implications for Urban Air Quality	8
Implications for Other Air-Quality Phenomena	9
Global Warming	9
Acidic Deposition	9
Aquatic and Terrestrial Environments	10
Groundwater	10
Aquatic Ecosystems	10
Terrestrial Ecosystems	11
Health and Safety Issues	11
Hazards Based on Exposure to Methanol	11
Fuel-System Hazards in Normal Operation	11
Fuel-System Hazards in Accidents	12
Fire Hazards	12
Regulatory Considerations	13

COMPRESSED NATURAL GAS VEHICLES	14
Introduction	14
Emissions and Air Quality	14
Emissions From Spark-Ignition Engines	14
Carbon Monoxide	14
Oxides of Nitrogen	14
Hydrocarbons	15
Aldehydes	16
Additional Testing Needs	16
Emissions From Compression-Ignition Engines	16
Hydrocarbons	16
Carbon Monoxide	16
Oxides of Nitrogen	16
Aldehydes	16
Particulates	16
General	17
Unresolved Technical Issues Affecting Emissions	17
Effects of Improperly Installed Conversion Kits	17
Emissions of Dual-Fuel Vehicles Operating on Gasoline	17
Compatibility of CNG Vehicles with Present Exhaust-Emission-Control Hardware	18
Cold Starting	18
Efficiency and Performance of CNG Vehicles Relative to Emissions	18
Low-Level Ozone-Reduction Potential of CNG Vehicles	18
Implications for Urban Air Quality	19
Implications for Other Air-Quality Phenomena	19
Global Warming	19
Stratospheric Ozone Depletion	20
Acidic Deposition	20
Health and Safety Issues	20
Health Risks	20
Fire Hazards Based on Fuel Properties	20
Fuel System Hazards in Normal Operation	22
Fuel Leakage	22
Corrosive Failure of CNG Cylinders	22
Fuel-System Hazards in Accidents	23
Control of Fuel Release on Impact	23
Control of Fuel Tank Rupture in Fires	23
Control of Passenger Compartment Intrusion	23
Dual-Fuel Systems Hazards	23
Hazards in Vehicle Refueling	24
Safety History of Natural Gas Vehicles	24
Public Safety Summary	24
Regulatory Considerations	24
Emission Regulations	24
Safety Regulations	25
 ELECTRIC VEHICLES	 26
Introduction	26
Emissions and Air Quality	26
Health and Safety Issues	27
Battery Manufacturing	27
Lead-Acid	27
Nickel-Iron	27
Sodium-Sulfur	28

Potential Hazards During Electric Vehicle Operation	28
Lead-Acid	28
Nickel-Iron	28
Sodium-Sulfur	28
Battery Recycling and Disposal	29
Lead-Acid	29
Nickel-Iron	29
Sodium-Sulfur	30

REFERENCES	R-1
------------------	-----

TABLES

1	Physical Properties of Methanol, Gasoline, and Diesel Fuel	2
2	Emissions From Methanol Use in Compression-Ignition Engines Relative to Diesel Fuel	5
3	Health Hazards of Selected Fuels	12
4	Estimated Tolerance Levels for Methanol (ppm)	12
5	Comparative Toxicity Ratings of Gasoline, Methanol, and Formaldehyde	13
6	Comparison of Emissions From CNG-Fueled Spark-Ignition Vehicles Relative to Conventional Gasoline-Fueled Spark-Ignition Vehicles	15
7	Summary of Exhaust Emissions From Fumigated CNG-Fueled Compression-Ignition Engines Relative to Diesel-Fueled Engines	17
8	Selected Properties of CNG, Gasoline, and No. 2 Diesel Fuel	21

FIGURES

1	Relationships Among the Elements of the DOE Alternative Fuels Assessment	vii
2	Effect of Alternative Fuels on Emissions	viii
3	Effects of Methanol Fuel on Engine Emissions	3
4	Ratio of Regulated Emissions to the 1991-93 Federal Standard for Diesel and Methanol Buses	4
5	Comparison of CMU/CARB and Sierra Projections of Year 2010 for Alternative Fuels	9
6	Relative Emissions of Carbon Dioxide Where Methanol Is Produced From Coal	10

INTRODUCTION AND EXECUTIVE SUMMARY

Purpose of This Report

The Department of Energy (DOE) is conducting a comprehensive technical analysis of a flexible-fuel transportation system in the United States—that is, a system that could easily switch between petroleum and another fuel, depending on price and availability. The DOE Alternative Fuels Assessment is aimed directly at questions of energy security and fuel availability, but covers a wide range of issues as illustrated in Figure 1. To keep interested parties informed about the progress of the DOE Alternative Fuels Assessment, the Department periodically publishes reports dealing with particular aspects of this complex study.

This report examines environmental, health, and safety concerns associated with a switch to alternative- and flexible-fuel vehicles (element 19 in Figure 1). Three potential alternatives to oil-based fuels in the transportation sector are considered: methanol, compressed natural gas (CNG), and electricity. The objective of the report is to describe and discuss qualitatively potential environmental, health, and safety issues that would accompany widespread use of these three fuels. These issues are quantified to the extent possible, though this is not a specific objective of this report. An environmental comparison will be conducted later in the assessment (element 21 in Figure 1), which will analyze quantitatively the environmental effects of different alternative-fuel vehicle scenarios.

Each of the fuel-specific chapters in this report presents the results of exhaustive literature reviews; discussions with specialists in the vehicular and fuel-production industries and with Federal, State, and local officials; and recent information from in-use fleet tests. Each chapter deals with end-use and process emissions of air pollutants, presenting an overview of the potential air pollution contribution of the fuel—relative to that of gasoline and diesel fuel—in various applications. Carbon monox-

ide, particulate matter, ozone precursors (oxides of nitrogen and volatile organic compounds), and carbon dioxide (from processing activities) are emphasized.

More general public health and safety issues are then introduced, emphasizing hazards due to physical and chemical properties of the fuels, both from normal operation (including refueling) and from accidents. Workers employed in producing each fuel or components for the associated vehicles may face additional or different hazards than those encountered by the public; such hazards are described where warranted. Finally, known and potential regulatory constraints on alternative-fuel distribution systems and use are discussed.

Ethanol derived from biomass is not treated explicitly as a fuel alternative in this report because it is generally similar to methanol from an environmental, health, and safety perspective. Virtually all issues identified in the chapter on methanol would be relevant to ethanol, except those related to production.

Methanol

Methanol, which can be produced from such feedstocks as natural gas and coal, burns cleaner than gasoline. Data on methanol vehicles are limited, but available information suggests that methanol is more environmentally benign than gasoline, as well as safer.

Environmental Concerns. Controlling emissions from methanol vehicles appears to depend on the development and use of a highly effective catalytic system in combination with appropriate engine maintenance. Additional testing under carefully controlled conditions should be performed to more accurately assess methanol's potential environmental effects. The existing data suggest the emission effects from the use of methanol illustrated in Figure 2.

In spark-ignition engines, methanol can be used either in dedicated vehicles or flexible-fuel vehicles (FFV's). Dedicated vehicles can

Figure 1 — Relationships Among the Elements of the DOE Alternative Fuels Assessment

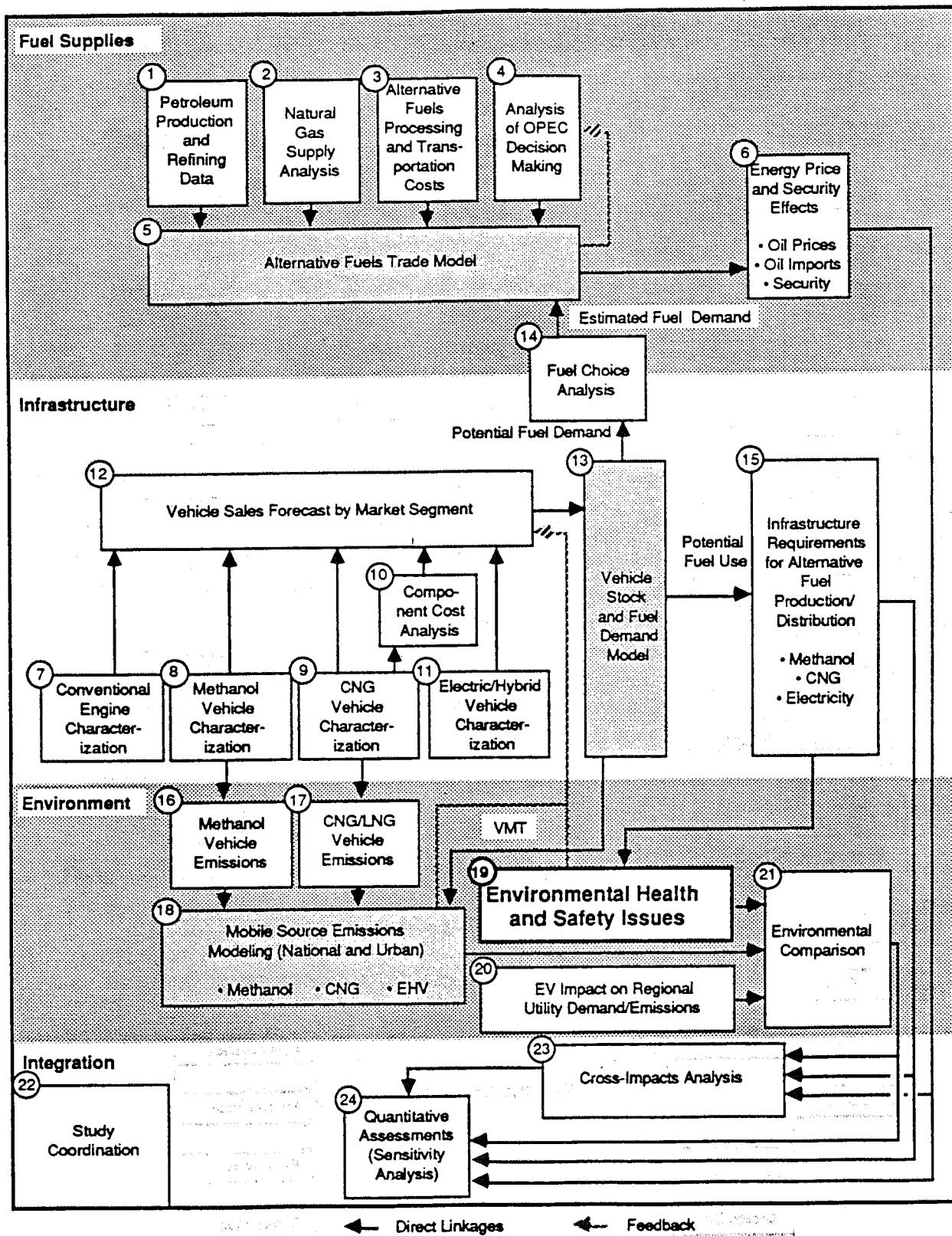
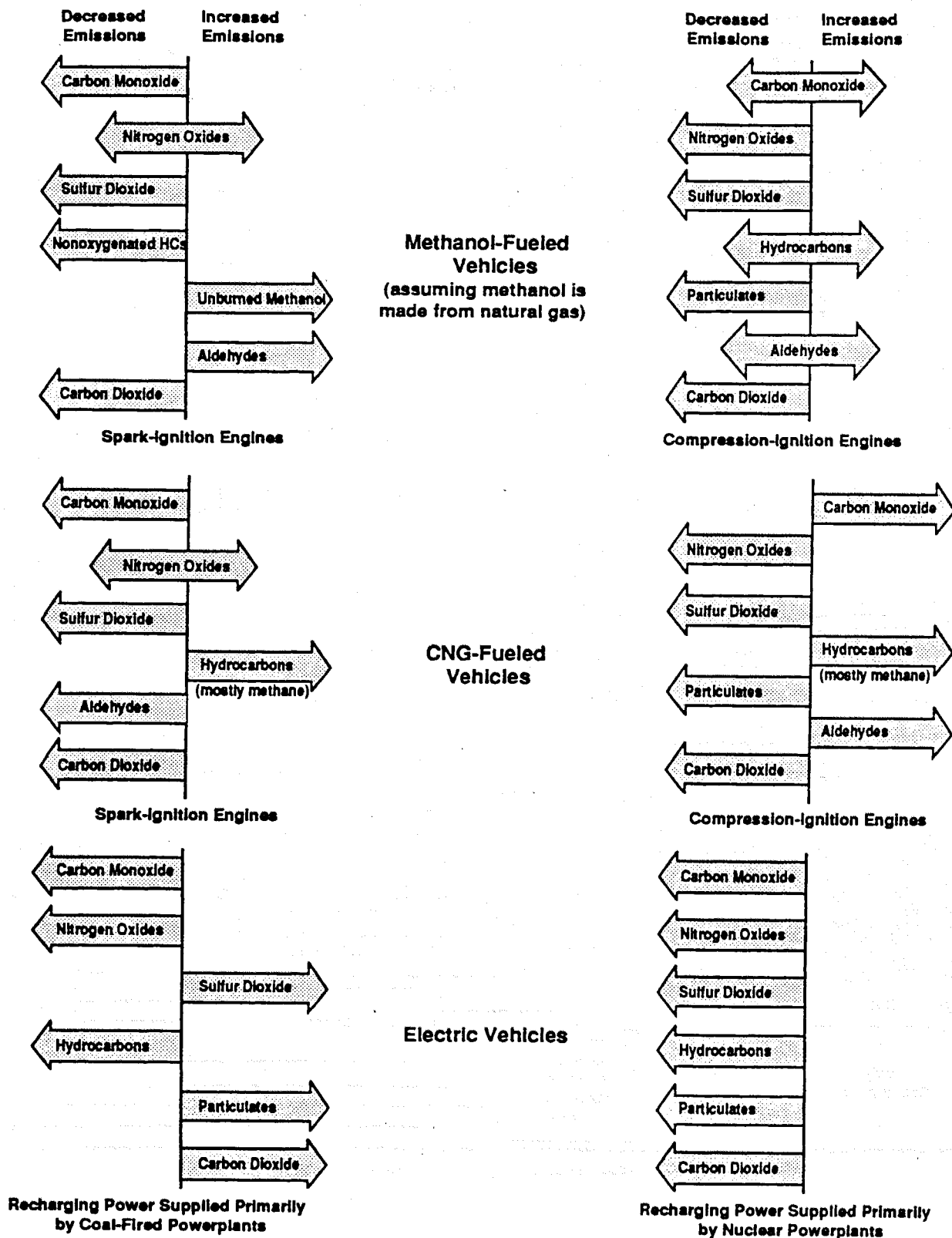


Figure 2 — Effect of Alternative Fuels on Emissions

Limited data suggest that the substitution of alternative fuels for gasoline and diesel fuels would result in the following changes in emissions:



use neat (100 percent) methanol or methanol blended with gasoline (up to 15 percent gasoline by volume). FFV's have been developed to use a range of methanol/gasoline blends, from 85 percent methanol/15 percent gasoline (M85) to 100 percent gasoline.

Carbon monoxide emissions from methanol-fueled spark-ignition engines usually are lower than those from gasoline engines. Aldehyde emissions (primarily formaldehyde) from methanol-fueled spark-ignition engines are much higher than those from gasoline engines. However, even though aldehyde emissions are potent contributors to ozone formation, the U.S. Environmental Protection Agency (EPA) has estimated that methanol is less prone to contribute to ozone formation than gasoline. This is because the unburned hydrocarbons from methanol-fueled spark-ignition vehicles contain fewer constituents that react photochemically to form ozone.

Focusing just on emissions, methanol-fueled spark-ignition engines seem to offer only a marginal improvement over gasoline engines. In compression-ignition engines, however, methanol has a clearer advantage. Although methanol-diesel blends are impractical (because these two fuels do not mix easily), many techniques have been developed for using neat methanol in compression-ignition engines. In general, nitrogen oxides and particulate emissions are lower compared to diesel-fueled vehicles, while hydrocarbon and carbon monoxide emissions depend on the specific technology being used. It is too early to draw firm conclusions, but the most environmentally promising technologies seem to be spark-assisted ignition systems or glow-plug ignition systems in conjunction with catalysts.

A significant advantage expected of methanol use in engines is its potential for reducing nitrogen oxide emissions relative to emissions from gasoline- and diesel-fueled engines. In addition, methanol contains no sulfur and does not contribute to atmospheric sulfur dioxide. Because emissions of nitrogen oxides and sulfur dioxide lead to acidic deposition, a switch to methanol-fueled vehicles would make a minor contribution to reducing acid rain.

Methanol-fueled vehicles can emit significant amounts of carbon dioxide—a major greenhouse gas—though these emissions are

slightly lower than carbon dioxide emissions from gasoline-fueled vehicles. Given that petroleum refining and the production of methanol from natural gas both produce comparable amounts of carbon dioxide, a switch to natural-gas-based methanol would have a small advantage in this regard. However, if the feedstock were coal, then carbon dioxide levels would increase. Carbon dioxide emissions from the production of methanol from coal far outweigh any benefits from methanol's lower carbon dioxide emissions from combustion.

Changing from gasoline to neat methanol may reduce the overall impact of fuels on aquatic and terrestrial environments. The impacts of methanol spills on drinking water and aquatic ecosystems are relatively milder, shorter, and more localized than for equal quantities of gasoline or diesel spills. Terrestrial ecosystems affected by a methanol spill will recover within weeks. Gasoline spills, in contrast, can cause extensive, long-term damage. However, for both aquatic and terrestrial ecosystems, a methanol-gasoline blend spill would have more severe impacts than would a gasoline spill, with the gasoline concentration determining the severity.

Health and Safety Concerns. Identified human illnesses from methanol exposure (through inhalation, ingestion, or skin contact) include organic solvent poisoning, systemic acidosis, and central nervous system effects. (The addition of odorants, such as gasoline, hopefully would prevent accidental ingestion.) Short-term exposures to methanol below certain threshold values do not pose major health hazards. Overall, gasoline is considered more hazardous to health than neat methanol, but methanol-gasoline blends pose a more serious hazard than either neat methanol or gasoline.

Other public risks posed by methanol use include fuel-system hazards during normal operation (though no long-term or permanent damage is anticipated); fuel-system hazards in accidents (in theory, a far less significant risk than gasoline); and general fire hazards. Neat methanol's ignitability in ventilated areas is between that of gasoline and diesel; in enclosed environments, it is flammable over a wide temperature range.

Compressed Natural Gas

As with methanol, emissions data for CNG vehicles with spark-ignition and compression-ignition engines are limited. However, available information suggests that CNG is more environmentally benign than gasoline. The efficiency and performance of CNG vehicles are possible concerns, particularly with dual-fuel retrofits—though there is evidence that dedicated, optimized CNG vehicles may have efficiency and performance levels equivalent to those of gasoline vehicles. No major shifts in health impacts are anticipated from CNG use.

Environmental Concerns. Total hydrocarbon emissions from spark-ignition (SI) CNG vehicles are generally higher than from their gasoline-fueled counterparts. However, these emissions are predominately methane, which is nonreactive, and therefore will contribute less to low-level ozone formation. Still, additional analysis is necessary to clarify CNG's overall potential in reducing low-level ozone. CNG use also changes the level of other ozone precursors (for example, NO_x).

CNG use in spark-ignition engines will reduce carbon monoxide emissions, largely as a result of better air-fuel mixing and lean combustion. Emissions of nitrogen oxides can decrease or increase with CNG use in SI vehicles. Actual emissions are highly dependent on spark timing, air-fuel mixture adjustments, and characteristics of the emission-control system. While data on aldehydes are extremely limited, one report concludes that formaldehyde levels from CNG generally are the same as or lower than levels from gasoline vehicles.

Relative to diesel-fueled vehicles, diesel vehicles converted to dual-fuel CNG-diesel operation, with fumigation, increase both hydrocarbon emissions (again, mostly nonreactive methane) and carbon monoxide emissions. Available test results do not indicate whether CNG vehicles would exceed the carbon monoxide or HC emission standards for compression-ignition engines. Alternatively, compression-ignition CNG vehicles can be designed to lower overall nitrogen oxide and particulate emissions relative to diesel-fueled vehicles. The power and performance tradeoffs are unknown. Formaldehyde emissions are not expected to pose problems with CNG-fueled compression-ignition engines.

As indicated, most of the hydrocarbon emissions from CNG vehicles are in the form of methane—a greenhouse gas. Even so, increased use of CNG as a vehicle fuel would reduce emissions of greenhouse gases relative to gasoline and, possibly, diesel. This is because CNG use would significantly reduce carbon dioxide emissions. According to one estimate, natural gas vehicles emit one-fourth less carbon dioxide than gasoline vehicles during vehicle operation.

Because CNG combustion produces no sulfur oxides, these vehicles (like methanol-fueled vehicles) would lead to a reduction in the relatively small contribution of mobile sources to sulfur oxide totals. An overall change in acid deposition precursors is difficult to estimate, however, because NO_x emissions may increase from SI CNG vehicles. Figure 2 provides a summary of the emission effects of CNG vehicles.

Health and Safety Concerns. Although methane, in sufficient quantities, is a simple asphyxiant, it is otherwise nontoxic and generally has significantly lower adverse health impacts than gasoline. However, the safety of CNG vehicles has yet to be resolved. One study concluded that gaseous fuels have higher relative risks in some cases, but are generally as safe as—and perhaps safer than—gasoline in other cases. Others have concluded that nothing appears to preclude the safe use of natural gas in vehicles.

Natural gas released from CNG tanks at ambient temperature is considerably less dense than air and will rise, diffuse, and disperse in unconfined spaces. In confined areas, however, flammable air-fuel mixtures could accumulate more readily than with gasoline, though considerably more natural gas must mix with the air to render the mixture combustible. Although methane seems less likely than gasoline to ignite, it poses more of a hazard once it starts burning. Methane flames are clean-burning, yellowish, and visible in daylight, but they are not as easily seen as gasoline flames. Methane air mixtures may also detonate. The detonability of these mixtures is influenced by whether or not they are confined.

Detailed accident data for natural gas vehicles are sparse. Within the existing data, few fire and explosion accidents have been reported.

Possible fuel-system hazards in accidents include fuel release on impact, fuel tank rupture in fires, and dual-fuel system hazards resulting from retrofits that are not completely compatible with the vehicle's design.

Leakage potential can sometimes be greater in gaseous fuel systems because of higher storage pressures and different chemical properties. Tank corrosion is also a safety concern in CNG vehicles—corrosive constituents of natural gas have caused catastrophic failure of steel cylinders used for bulk transport and storage. To address corrosion the Department of Transportation (DOT) regulates cylinders used in commercial shipment of gas. DOT has concluded that the use of cylinders meeting these regulations may not be adequate for the more severe operating conditions that would be encountered in CNG vehicle use. Such cylinders are, however, more rugged than gasoline tanks and can better withstand accidents. Lightweight CNG tanks developed in the early 1980's for vehicle use might be more vulnerable to collision damage.

Electric Vehicles

Although most observers believe that use of electric vehicles will benefit the environment, the batteries used in these vehicles could entail health and safety problems, depending on what materials are chosen.

Environmental Concerns. Electric vehicles (EV's) themselves produce virtually no emissions. Thus, unlike vehicles powered by onboard combustion of various fuels, they produce no street-level pollutants, with the removal of carbon monoxide probably being the most significant local benefit. A switch to electric vehicles, however, would not necessarily eliminate vehicle-related emissions. Rather, it would concentrate those emissions at the powerplants that supply the electricity used to recharge the vehicles' batteries, and the actual emissions would depend on the type of powerplant.

On the one hand, if the electricity were generated at poorly controlled fossil powerplants, the pollutant concentration in the area of the powerplant could increase significantly. On the other hand, the use of nuclear, wind, hydropower, or solar power would virtually eliminate vehicle-related air pollution. If well-controlled

coal-fired powerplants were the dominant source of electricity, then increased use of electric vehicles would probably reduce emissions of hydrocarbons, carbon monoxide, and nitrogen oxides; but it would increase emissions of sulfur oxides, particulates, and greenhouse gases. Alternatively, if the baseload power were primarily nuclear, there would be an even greater reduction in nitrogen oxides and a decline in particulates, sulfur oxides, and greenhouse gases. Figure 2 provides a summary of emission effects of EV's.

Health and Safety Concerns. Three types of batteries have been considered for use in electric vehicles—lead-acid, sodium-sulfur, and nickel-iron—and each involves different health and safety issues.

The toxicity of lead is well known, and public and occupational exposure to lead are the principal safety concerns with lead-acid batteries. The Occupational Safety and Health Administration and EPA are considering a further tightening of current standards regarding permissible levels of lead—both in the air and in the blood. Releases of arsine and stibine (two poisonous gases), hydrogen explosions, sulfuric acid burns, and electric shock are all operational hazards related to the use of lead-acid batteries; each type of hazard is serious, but none is difficult to overcome. Although most lead-acid batteries are expected to be recycled, increased use of these batteries could result in the uncontrolled and random disposal of millions of pounds of toxic and acidic materials.

Health issues are minimal for sodium-sulfur batteries; the main focus is on public safety, especially avoiding sodium fires, sodium-water explosions, and runaway sodium-sulfur reactions. Sodium and sulfur react violently in direct contact. In assembled cells, sodium and sulfur are separated only by fragile tubes of beta alumina; however, cell designs have greatly reduced the chance of a single cell failure resulting in failure of adjacent cells. The ability of sodium-sulfur batteries to withstand minor accidents without serious sodium reactions is unknown. The relatively low value of materials in spent sodium-sulfur batteries suggests that these batteries will be discarded rather than reprocessed. A battery purchase "deposit" might be necessary to prevent the illegal and unsafe dumping of these batteries.

The nickel-iron battery presents significantly lower health and safety hazards than lead-acid or sodium-sulfur, with the main concern being the safe handling of the copious amounts of hydrogen created during battery charging. Providing adequate ventilation during recharge is necessary to reduce the likelihood of explosion and injury. The principal emissions from the manufacture of nickel-iron batteries are airborne dust, vapor, and wastewater effluent. However, these hazards are clearly less serious than hazards associated with lead-acid batteries. Overall, nickel-iron batteries appear to be quite safe under normal operating condi-

tions. It is reasonable to assume that nearly all spent nickel-iron batteries will be collected to recover more than 99 percent of the valuable nickel.

This report reflects the state-of-knowledge as of June 1989. Where specific findings subsequent to that date modify the original description of the issues discussed in this report, an effort has been made to qualitatively update that description. However, the quantitative component of any such discussion remains unchanged.

METHANOL VEHICLES

INTRODUCTION

This section addresses the potential environmental, health, and safety (EH&S) effects of vehicles that run on methanol, either in the form of neat methanol (M100) or mixed with gasoline (for example, M85).

Methanol is a clear, colorless liquid with a faint odor. It has the lowest molecular weight of the aliphatic (straight-chain) alcohols. Methanol can be produced from a variety of feedstocks, including natural gas and coal. As a useful solvent, methanol is used extensively in the manufacture of organic intermediates. Methanol tends to absorb moisture and blends with water to form homogeneous solutions. Methanol dissolves readily in other alcohols and chlorinated hydrocarbons, but has limited solubility in diesel fuel, vegetable oils, and aliphatic hydrocarbons.

The properties of neat methanol compared to gasoline and diesel fuel are presented in Table 1. The stoichiometric air/fuel ratio of methanol is about 50 percent that of gasoline, meaning that twice the mass of methanol per unit mass of air is required to achieve roughly the same energy release from combustion. The 7- to 36-percent flammability limit of methanol in air and its faster flame speed permit more efficient burns in lean mixtures, resulting in a more useful release of heat from combustion with reduced heat-transfer losses. While efficiency improvements theoretically may reach 30 percent, tradeoffs with emission constraints may limit this value to 15 to 20 percent. Methanol's high autoignition temperature, relatively low vapor pressure (4.6 pounds per square inch at 100°F), and high flash point (52°F) are expected to make it safer than gasoline. Water-methanol mixtures with as little as 21 percent methanol by volume are flammable.

EMISSIONS AND AIR QUALITY

Emissions from Spark-Ignition Engines

Two types of methanol-fueled vehicles with spark ignition (SI) engines are currently being developed. Dedicated methanol-fueled vehicles are designed to operate only on methanol, though the fuel may include other components (for example, 85 percent methanol/15 percent gasoline). Flexible-fuel vehicles (FFV's) are capable of operating on methanol, gasoline, or any mixture of the two. Advanced dedicated vehicles will likely use neat methanol in lean-burning (that is, containing a relatively higher amount of oxygen), high-compression engines with advanced fuel injection. Flexible-fuel vehicles will incorporate systems to determine fuel composition and make appropriate adjustments to ensure efficient combustion.

Emission data for FFV's are extremely limited. Therefore, the discussion below focuses on dedicated vehicle emissions (using M100 or M85), for which there is more information. Where available, assessment of FFV emissions is provided.

Factors Affecting Emissions. When methanol is used in place of gasoline as a transportation fuel, engine-out emissions are determined by the same set of parameters governing gasoline. These include fuel composition, air/fuel ratio, engine design and operational efficiency, driving conditions for specific vehicles, and quality of vehicle maintenance. Total tailpipe emissions are also governed by the nature and efficiency of downstream emission control devices. Control of emissions from methanol vehicles appears to depend on the availability and use of a highly effective catalytic system in combination with appropriate engine maintenance.

The high oxygen content of methanol relative to that of gasoline requires a change in the air/fuel ratio from 15.5 to 6.4. For a meaningful comparison of the two fuels, emissions are thus related to an air/fuel equivalence ratio. A

Table 1 — Physical Properties of Methanol, Gasoline, and Diesel Fuel

Property	Methanol	Gasoline ^a	Diesel Fuel ^b
Formula	CH ₃ OH	Mixture of C ₆ to C ₁₄ hydrocarbons	Mixture of C ₁₂ to C ₂₀ hydrocarbons
Specific gravity at 60°F	0.796	0.70–0.78	0.80–0.88
Density at 68°F (lb./gal.)	6.60	5.8–6.5	6.7–7.3
Initial boiling point range (°F)	148	80–120	375–425
Vapor pressure at 100°F (psi)	4.63	7–15	Negligible
Flash point minimum (°F)	52	-45	100 ^c
Autoignition temperature (°F) ^d	867	450–900	400–500
Flammability limits (vol. % in air)			
Lower	6.7	1.4	—
Higher	36.0	7.6	—
Heating value at 68°F (Btu/gal.)			
Lower	56,560	115,400 (avg.)	129,500 (avg.) ^e
Higher	64,250	124,800	—
Stoichiometric mass air/fuel ratio	6.45	14.4–15.0	15.0 (avg.)
Energy (Btu/ft ³ of standard stoichiometric mixture at 68°F)	92.5	94.0	97
Latent heat of vaporization at 68°F (Btu/lb.)	506	150	100–200
Octane number			
Research	106	91–98	—
Motor	92	82–92	—
Cetane number	—	—	45–55
Sulfur content (wt. %)	0	0.020–0.045	0.20–0.25

^aCompiled from Obert (1968).

^bCompiled from NOAA (1977).

^cFlash point for No. 1 diesel is 100°F; No. 2 diesel is 125°F.

^dVaries greatly with testing set-up and procedure; values

obtained from Perry et al. (1977) and National Fire Protection Assn. (1977).

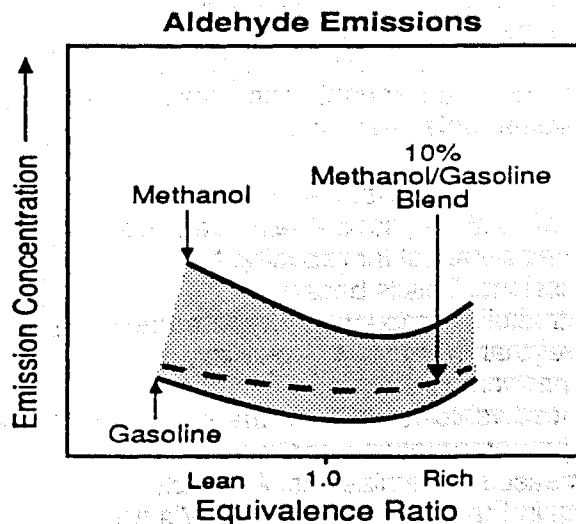
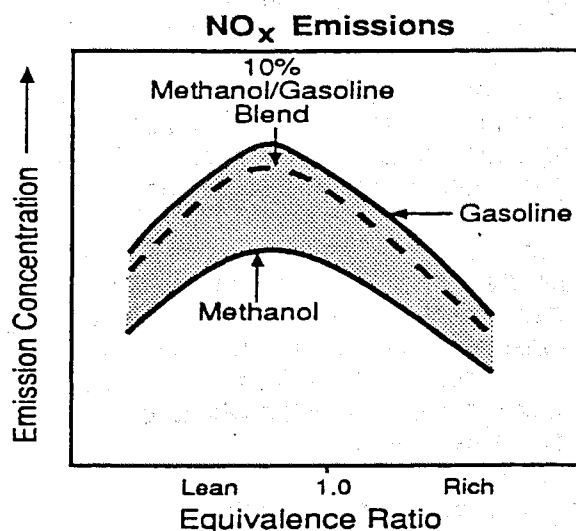
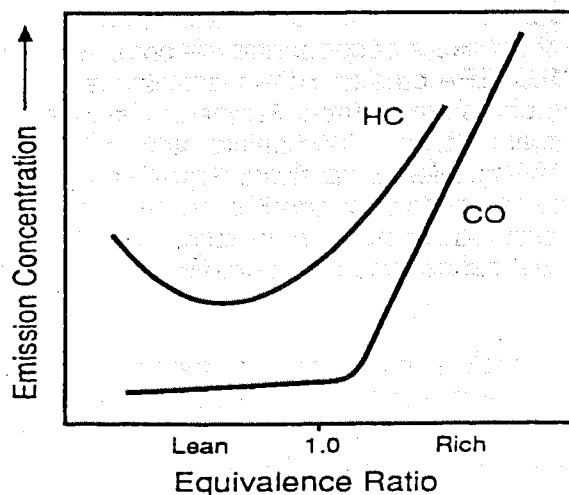
^eEstimated using average API gravity from Shelton (1979) and National Bureau of Standards estimates of combustion heats.

review of the basic interactions between fuel use and primary operating conditions in a homogeneous-charge, SI, Otto-cycle engine reveals several relationships between the air/fuel equivalence ratio and the design characteristics of internal combustion engines (Singh and Sekar 1988). As seen in Figure 3, methanol's leaning effect significantly reduces CO, HC, and NO_x, all of which are quite sensitive to the air/fuel ratio. At the same air/fuel equivalence ratio (for example, when the air/fuel mixture is adjusted after a blend has been introduced into the vehicle), emissions and fuel economy are comparable to those of the gasoline engine. The greatest emission reductions are in the fuel-rich region, primarily because of methanol's leaning effect. (The leaning effect of methanol-gasoline blends, which has been observed in present-technology vehicles, may be significantly different in future vehicles that have feedback control and adaptive learning (Schiller 1989).)

Hydrocarbons. The unburned HC's from methanol vehicles consist primarily of unburned methanol and other oxygenates. With the exception of the aldehydes, oxygenates are significantly less reactive in the formation of ozone than the nonmethane HC in gasoline vapors and exhaust. EPA estimates that methanol as a vehicle fuel has less ozone-forming potential (due to its lower content of reactive constituents) than does gasoline. According to EPA, exhaust emissions of VOC's, when adjusted for the relative reactivities of their constituents, will be lower from all types of methanol fuels (gasoline-methanol mixtures of varying percentages and neat methanol) than from gasoline (EPA 1988). They will be 80 percent lower with neat methanol and up to 40 percent lower with FFV's operating on M85. This view is supported by Carter et al. (1986). Even methanol vehicles with higher total HC might thus be expected to contribute less to ozone formation relative to gasoline vehicles.

However, some test results show that total emissions of the more highly reactive, ozone-forming nonmethane HC's (NMHC's) from methanol vehicles are almost as high as these emissions from current best-technology vehicles using petroleum fuels. Ford Motor Company recently reported that non-oxygenated organic compounds from both M85- and M100-fueled vehicles are about

**Figure 3 — Effects of Methanol Fuel on Engine Emissions
CO and HC Emissions**



Source: Singh and Sekar 1988.

0.25 grams per mile (Nichols 1988), which is comparable to the emissions from gasoline vehicles. Sapre (1988) of the General Motors Corporation confirmed the fact that emissions of these HC's occur during the combustion of M100. EPA data on HC's were estimated rather than measured. Further, most of the earlier data on M100 vehicles were taken with very low mileage catalysts. More testing under carefully controlled conditions should be performed to assess more accurately the actual ozone reduction benefits of methanol use.

Evaporative emissions from methanol-fueled flexible-fuel vehicles are higher than those from gasoline vehicles, but still below the Federal standard of 2 grams per test.

Aldehydes. Aldehyde emissions (primarily formaldehyde) from methanol engines increase by an order of magnitude over those from gasoline engines (Gabele et al. 1985). Recent tests have confirmed these results (Singh and Sekar 1988). It is expected that the higher aldehyde emissions may be controlled by varying the catalyst placement. The extent of that control may depend on the age of the catalyst and the methanol fuel content. Preliminary results from studies at the Ford Motor Company indicate higher emissions of formaldehyde (and methanol) from M100 than from M85 fuels in vehicles with aged catalysts (Nichols 1988).

Carbon Monoxide. CO emissions from dedicated methanol vehicle engines usually are lower than from comparable gasoline-fueled engines. Available data indicate that CO emissions from FFV's are roughly comparable to gasoline-fueled vehicles.

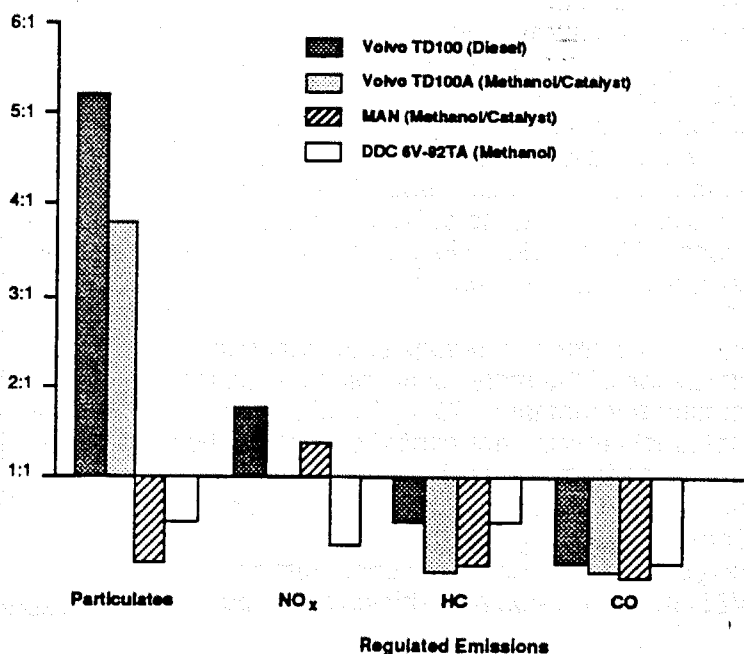
Oxides of Nitrogen. A possible benefit with methanol-fueled vehicles is their potential for reducing NO_x emissions. This is because methanol's combustion temperature is lower than gasoline's. However, the higher compression engines in advanced vehicles would operate at higher temperatures and would increase NO_x emissions. Available data indicate that NO_x from FFV's are roughly comparable to gasoline.

Methyl Nitrite. A recently identified concern (Ito et al. 1982) is that methanol emissions may react with atmospheric NO_x to produce methyl nitrite (CH₃NO₂), which has proved toxic to laboratory animals but remains to be evaluated for its effects on humans.

Emissions From Compression-Ignition Engines

The most significant benefits of methanol fuel probably are achieved with compression-ignition (CI) engines. Despite its extremely low cetane number, methanol provides a degree of improvement in emissions and possibly power (Alson and Baines 1982; Ecklund et al. 1982), making it attractive for use in a modified CI engine or as a diesel fuel replacement (Gopalakrishnan and Balasubramanian 1982). Figure 4 presents ratios of regulated emissions from a variety of comparable engines, using the 13-mode test (which originally was defined by EPA for heavy-duty vehicles) compared to the 1991-93 Federal standard using the transient test (which EPA now uses). The transient test was chosen as a base because its requirements are more stringent than those of the 13-mode test.

Figure 4 — Ratio of Regulated Emissions to the 1991-93 Federal Standard for Diesel and Methanol Buses



**Table 2 — Emissions From Methanol Use in Compression-Ignition Engines
Relative to Diesel Fuel**

Tested System	CO	NO _x	HC	Particulates	Aldehydes
Stabilized emulsions	0/+ ^a	+	+	-	NR
Fumigation	+	-	+	-	NR
Dual injection					
Noncatalytic	+	-	+	-	+
Catalytic	-	-	-	-	+
Spark-ignition	- ^b	- ^b	- ^b	- ^b	NR
Ignition-improving additives	+	+/-	+	NR	NR
Glow plugs or surface ignition	+	-	+/- ^a	-	+/-

^aDepends on load.

^bVaries with load; full load shown here.

+ = Increased emissions

- = Reduced emissions

+/- = No consistent direction of change in emissions

0 = No effect on emissions

NR = Not reported

Source: Singh and Sekar (1988).

Numerous techniques have been developed to use methanol in CI engines, particularly those in heavy-duty vehicles and buses. Table 2 summarizes the emission characteristics of the different approaches relative to engines that use diesel fuel. Brief descriptions of the approaches relevant to this study are provided in subsequent sections. Some approaches require minimal changes to diesel engines, while others require significant modifications to combustion, fuel, and associated system parameters. In general, NO_x and particulate emissions are lower when using neat methanol in CI engines than when using diesel fuel, while HC and CO emissions depend on the specific technology (though increases to date are within applicable standards). Aldehyde emissions are an area of concern, particularly during warmup and idle. Further evaluation of engines optimized for use with neat methanol is necessary.

Methanol-Diesel Fuel Emulsions. The solubility of methanol in the vast majority of diesel fuels is practically zero without the use of significant amounts of cosolvents. Methanol-diesel blends therefore are not being pursued as practical alternatives. Emulsions, however, are an option.

In an emulsion, the methanol is suspended as droplets in the diesel fuel. Varied data from limited tests led Singh and Sekar (1988) to conclude that emission levels from direct injection of methanol-diesel emulsions depended on the methanol content of the fuel and on engine load. CO emissions generally were unchanged except under full load and were lower even at full loads when equivalence ratios were kept lean (that is, the injector size was not adjusted). Emissions of NO_x were higher than those of diesel fuels, and HC emissions increased—particularly at partial loads.

Stabilized emulsions may require expensive emulsifiers. They also may exhibit poor low-temperature performance.

Ignition-Improving Additives. Ignition-improving additives tend to increase CO and HC emissions, particularly at low loads. While the effect of additives on NO_x emissions tends to vary, recent developments at Daimler-Benz have produced a significant reduction in NO_x and a complete removal of soot (Hardenberg 1987).

The Cummins Engine Company has developed a CI engine using additives such as Avocet (Duggal and Welch 1988). Minimal engine changes were required. While performance characteristics and fuel economy are comparable to the Daimler-Benz results, emission-control technology requires further development.

Ignition-improving additives may be expensive and also may require the use of a larger fuel pump, additional lines, and injectors to meet full-load requirements. Further, these additives may introduce unexpected pollutants into the atmosphere.

Spark-Assisted Ignition. Neat methanol is used in this system. With neat methanol, CO emissions are dependent on the engine load, with the lowest emissions occurring at higher loads. Catalysts tend to lower both CO and HC emissions. While the levels of unburned fuel tend to increase, NO_x and particulate emissions tend to be lower than in diesel engines. Possible drawbacks of this system are that spark-assisted ignition requires additional space for spark plugs in the cylinder head of a CI engine and that the vehicle may still exhibit poor cold-starting and decreased range.

Glow-Plug and Surface-Ignition. Neat methanol in noncatalytic glow-plug or surface-ignition engines (SIE's) produces more CO, unburned fuel, and aldehydes than are produced by diesel fuel, while NO_x and particulates generally are reduced over the engine's load range. (The particulates are thought to come from lubricating oil swept into the exhaust of the two-stroke engine during scavenging.)

The use of catalysts can alter the emission characteristics of glow-plug engines and SIE's. Recent developments indicate that unburned methanol and formaldehyde emissions may be reduced by catalytic converters (McCabe et al. 1987). Overall, it appears from the limited data available that glow-plug ignition of alcohols in conjunction with catalysts can significantly reduce emissions of CO, HC, particulates, and aldehydes. However, these systems have yet to achieve the performance, reliability, and durability of conventional diesel engines. Glow-plug or SIE techniques have high energy requirements, and the durability of glow plugs and hot surfaces has not yet been verified.

In-Use Performance. The development of most of these modified engine concepts has been in such countries as Brazil and New Zealand, and few emission data have been collected. Vehicles that have attracted the most attention in the United States are the 6V-92 TA transit bus engine, developed by the Detroit Diesel Corporation (DDC), and the methanol D2566 FMUH bus engine, developed by MAN, a German organization.

The two-stroke DDC engine controls the scavenging air flow to maintain temperatures appropriate for methanol combustion. At light loads, this is supplemented by glow-plug ignition. The relatively complex control system probably was the cause of the high emissions of unburned fuel and CO in early engines. Only slight improvement relative to conventional diesel engines is seen in newer models. In addition, catalyst systems have not performed as well on DDC methanol engines as on MAN engines. The lower exhaust temperature and higher volume of unburned fuels call into question the ability of the two-stroke DDC engine to achieve the required limits on emissions.

The MAN engine, which uses a conventional spark-ignition system and a catalytic converter, has demonstrated consistently low emission characteristics in tests with transit buses. NO_x emissions, however, seem to be higher than those of the DDC methanol engines. Caterpillar and a few other engine manufacturers currently are developing newer versions of the four-stroke MAN engine to control HC's, CO, and formaldehyde.

Unresolved Technical Issues Affecting Vehicle Emissions

Data in the Singh-Sekar report (1988) include test results on small fleets and single vehicles. Before methanol vehicles can enter actual service, the concerns outlined in the following subsections must be addressed.

Engine Life and Maintenance. Methanol burns cleaner than gasoline but provides poor lubricity; however, the development or use of suitable lubricants may remedy this situation. FFV's have exhibited problems with carburetors and fuel-injector systems, which in turn have led to rapid emission control deterioration. Increased knowledge of proper maintenance should reduce the incidence of such failures. Alternatively, frequent overhauls may be required. Limited data on vehicles driven by Ford indicating that parts may need to be replaced less frequently than with gasoline must be verified, as must data indicating an overall net reduction in the life-cycle costs of methanol vehicles in comparison with gasoline-powered vehicles.

Changes In Components and Control Systems. To ensure optimal emission levels, flexible-fuel vehicles will need a fuel-composition sensor. In addition, more than one set of calibrations should be available for fuel and spark timing, particularly if gasoline and methanol are used alternatively. Significant additions to the microprocessor memory will be required to enable the interpolation routine for gasoline/alcohol mixtures. Oxygen-sensor modifications will be required to adjust for methanol's lean shift.

Emission-control systems also must be developed. The current evaporative emission controls used in gasoline vehicles may be inappropriate for methanol-gasoline mixtures, and changes in both tailpipe and evaporative emission control systems may be required.

Tailpipe emission controls would be affected primarily by aldehyde emissions during cold-weather operation with methanol. Approaches to control aldehyde emissions include revised catalyst formulations, enhanced engine warm-up rates, and catalyst heating for faster "light-off" (the point at which the catalyst becomes capable of controlling the emissions to desired levels). It is not yet apparent whether revised catalyst formulations would adequately ad-

dress the aldehyde emissions problem, but faster warmups should improve cold driveability.

Methanol's lean shift could result in oxygen-sensor problems and consequently affect emissions. Evaporative emission controls would require changes, including larger canisters and related purge-control systems. On-board controls, if implemented, would require larger canisters in all vehicles. Controlling unburned alcohol emissions would require additional controls.

Durability of Emission-Control and Fuel Systems. Although alcohols burn cleanly, the durability of emission-control systems appears questionable (Moses and Saricks 1987). Federal fleets have exhibited fuel-injector plugging, causing miscalibrated injection and catalyst overheating, which, in turn, increased emissions of NO_x, CO, and HC's. This could cause deterioration of emission-control systems over time. Heavy-duty CI engines have demonstrated particulate emissions in excess of standards caused by lubricating oil burnoff in the cylinders, indicating the possible need for particulate traps.

In addition, endurance tests by Daimler-Benz have shown fuel-related durability problems (Hardenberg et al. 1987). Serious cavitation-induced erosion has been observed in the injection system, and hard ceramic-type combustion deposits have resulted in increased wear, which could lead to premature failure and increased emissions. However, modifying engine parts and using lubricants may correct these problems.

Stock gasoline fuel systems used with methanol also have failed because of corroded metallic components and embrittled elastomeric materials. While early attempts by Ford to avoid these problems were expensive (Nichols 1985), inexpensive corrective measures likely are being developed, so the problems of premature failure and uncontrolled emissions may become less significant.

Cold Starting. Methanol-fueled flexible-fuel vehicles can be difficult to start and drive in cold weather (Nichols 1985, 1986). Methanol's low vapor pressure causes excessive cranking and, consequently, increased fuel flow; as a result, emissions at starting can be particularly rich in methanol. In addition, unconfirmed

reports of engine fires during cold starting have been noted in at least one test fleet. However, if the recently developed (but as yet undisclosed) solution by Ford is adequate, such problems and hazards may be a moot point, although the increased formaldehyde emissions under cold-engine idle conditions would still require appropriate emission-control technologies.

Hot Starting. The high boiling point of methanol relative to that of gasoline may result in a hot starting problem. Parking a methanol-fueled vehicle after it has operated at high ambient temperatures may cause vapor lock in the fuel line (Francis and Peters 1980), which may increase evaporative emissions.

Fuel Distribution System Emissions

Evaporative emissions during the transportation, storage, dispensing, and use of methanol as a transportation fuel are relatively low (approximately midway between gasoline and diesel fuel) but increase with methanol-gasoline blends. Although nearly twice as much methanol by volume is required to achieve the same operating range as gasoline, evaporative losses from neat methanol distribution could be about two-thirds those of gasoline. Because methanol-gasoline blends tend to alter the Reid Vapor Pressure of fuels, evaporative emissions may be controlled by adjusting fuel specifications and modifying vapor-recovery systems used both in vehicles and throughout the blend-distribution system (Bevilacqua et al. 1980).

Implications for Urban Air Quality

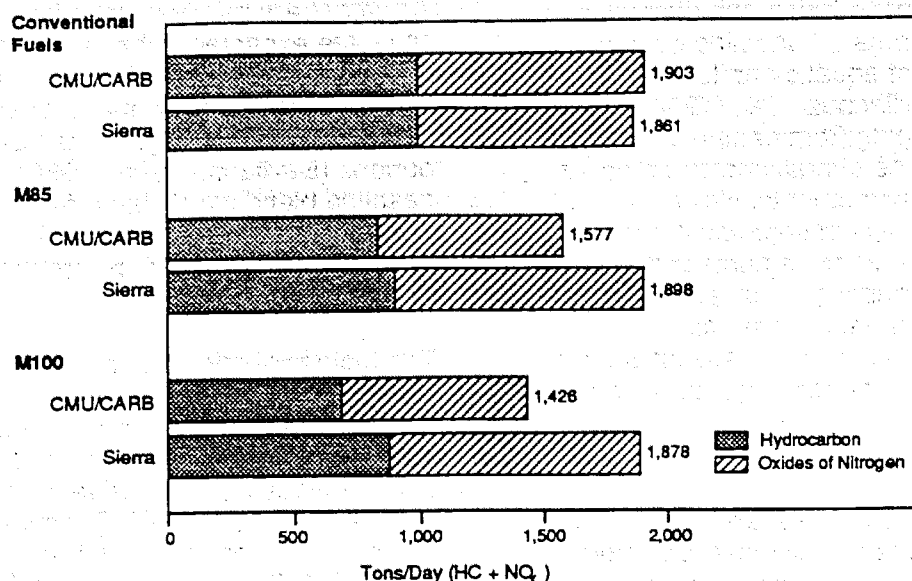
In general, EPA estimates that methanol (because of its lower content of reactive constituents) is less prone than gasoline to form ozone. This is in spite of the fact that aldehyde emissions, which are relatively photoreactive, are potent contributors to low-level ozone formation. When exposed to sunlight, they split into chemical species that eventually contribute to ozone formation (Jet Propulsion Laboratory 1983; Carter et al. 1986). Overall, if formaldehyde levels are kept sufficiently low—possibly through the use of catalysts—substituting methanol for gasoline appears to have no adverse effect on ozone levels. However, it may be difficult to keep aldehyde levels low, particularly during cold starting.

Opinions vary on the extent of the impact of methanol vehicles on ozone. Two papers from Carnegie Mellon University (CMU), which are based on California Air Research Board (CARB) assumptions in two computer-modeling studies, present an optimistic outlook for methanol (Harris and Russell 1988; Russell and Harris 1988). The CMU papers assume that M100 vehicles will emit no nonmethane hydrocarbons. Furthermore, they assume that formaldehyde emission levels can be controlled to 3 milligrams per mile in actual production vehicles. NO_x emissions from methanol vehicles are assumed to be as low as those from advanced-technology gasoline-fueled vehicles. All new vehicles starting with the 1990 model year are expected to be capable of using methanol. In addition, the CMU study used the CARB assumption that all petroleum refineries in southern California would be shut down as motor vehicles were converted to methanol and that off-road vehicles, for which conversion to methanol would be expensive, would be using methanol very soon. Another CARB assumption used is that all stationary sources (such as factories and refineries) will achieve NO_x reductions through methanol use. The results are shown in Figure 5. CMU estimates a reduction of up to 25 percent in ozone precursor emissions with the use of methanol.

The papers' estimates of emission characteristics, however, appear to be inconsistent with the available data base. Using more realistic assumptions, such as 1995 instead of 1990 for the feasibility of widespread methanol vehicles, as well as NMHC emissions 50 percent lower than advanced-technology gasoline vehicles, Sierra Research has projected different emissions results (Sierra Research 1989). They estimate at most a 1-percent reduction (Figure 5). Further assumptions in the Sierra approach include methanol NO_x emission factors at twice the levels projected for advanced-technology gasoline vehicles; the exclusion of off-road vehicles in the methanol-related emission reductions, at least in the near future; the continued operation of southern California refineries; and no emission reduction from stationary sources as a result of conversion to methanol.

The marginal changes in emissions from methanol spark-ignition (SI) engines relative to SI gasoline engines illustrated in the Sierra report raise serious questions about the need

Figure 5 — Comparison of CMU/CARB and Sierra Projections of Year 2010 for Alternative Fuels



for changing to methanol. Clearly, additional testing under carefully controlled conditions should be performed to more accurately assess methanol's environmental benefits in these engines.

Environmental gains are not yet reliably proven with methanol CI engines either. The limited data that exist on emissions from methanol compression-ignition (CI) engines compared to diesel CI engines favor methanol-type fuels. A dedicated, optimized methanol-fueled CI vehicle with a suitable catalytic converter may emit less reactive HC's, NO_x, and CO than would a comparable diesel-fueled vehicle. However, as discussed above, emissions from such vehicles will depend on the catalyst's effectiveness as well as on such factors as fuel stoichiometry, engine design, compression ratio, and timing. Thus, the lack of sufficient data makes it impractical, at this time, to expect motor-vehicle manufacturers to make the relatively expensive changeover to modified diesel engines.

Implications for Other Air-Quality Phenomena

Global Warming. Because of the current concern over greenhouse gases, the impact of methanol use on the emission of carbon dioxide (CO₂) also should be considered.

Emissions of CO₂ are not regulated by the Environmental Protection Agency (EPA). Although methanol combustion is relatively clean, the emitted CO₂ can be significant, as seen in Figure 6. CO₂ emissions from methanol-fueled internal-combustion engines are slightly lower than from gasoline-fueled engines. However, CO₂ emissions from the production of methanol—particularly when the primary feedstock is coal—far outweigh these benefits. Production of methanol from natural gas is expected to produce CO₂ at levels comparable to those from petroleum-refining operations.

The CO₂ emissions considered here relate only to combustion stoichiometry and a nominal component (about 10 percent) for fuel production. They do not include emissions from the mining or transporting of coal.

Acidic Deposition. Methanol contains no sulfur and does not contribute to atmospheric sulfur dioxide (SO₂). Thus, relative to conventional fuels, use of methanol vehicles would lead to a reduction in mobile-source related SO_x totals. Methanol vehicles may be calibrated to emit less NO_x, which would also reduce mobile-source-related ozone precursors.

AQUATIC AND TERRESTRIAL ENVIRONMENTS

Although the transportation and distribution of methanol and methanol-gasoline blends are expected to affect aquatic and terrestrial ecosystems, Bevilacqua et al. (1980) estimated that changing from gasoline to methanol may reduce the overall impact on aquatic and terrestrial environments. However, Machiele (1987) also assembled a comprehensive summary of the impacts of methanol fuels on aquatic and terrestrial ecosystems and perceived a more severe impact from gasoline-methanol blends. These issues are reviewed briefly in the following subsections.

Groundwater

Underground storage tanks are a significant source of groundwater contamination from gasoline and diesel fuels. However, the aerobic and anaerobic degradation rates of methanol and its tendency to disperse rapidly in water minimize the possibilities of toxic contamination (greater than 1,000 parts per million) of the drinking-water system (Machiele 1987). Bevilacqua did not project a significant environmental concern resulting from methanol spills.

Aquatic Ecosystems

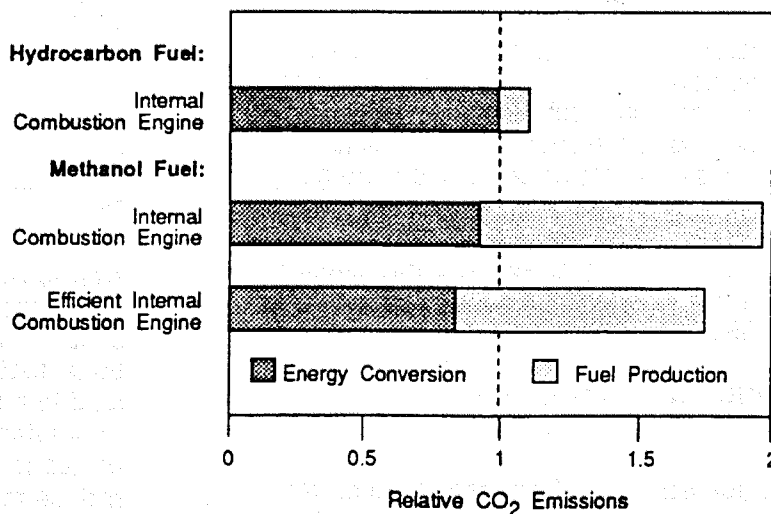
The rapid miscibility of methanol with water and its relatively rapid biodegradation under appropriate conditions render the impacts of methanol spills less severe and of relatively shorter duration than those of gasoline or diesel spills. While methanol concentrations may be toxic to specific aquatic species (0.5 percent can produce narcosis in many aquatic life forms), diluting a methanol spill, which is relatively easy, would reduce its impact. Furthermore, methanol's relatively rapid biodegradation under suitable conditions lessens its impact by significantly reducing the recovery time (Scott 1987).

D'Eliscu (1977) comments that, in general, methanol spills in marine and freshwater environments where concentrations exceed 1 percent are relatively localized. Moderate spills are expected to have minimal consequences because of methanol's solubility and biodegradability. In contrast, gasoline and diesel spills affect larger areas over longer periods (Bevilacqua et al. 1980). A methanol-gasoline blend would have more severe impacts than would a gasoline spill, with the gasoline concentration determining the severity (Machiele 1987).

The biological effects of a spill or leak are influenced by factors such as the scale and duration of the spill, tidal changes, temperature, oxygen availability, potential synergism, and the types of flora and fauna involved (Bevilacqua et al. 1980). Examples of some of these impacts are found in the literature (SMFTC 1982, 1986).

Bevilacqua also described the impact of methanol spills in freshwater systems. Critical factors include the amount and duration of the spill, water volumes and flow rates, temperature, oxygen availability, nature of affected species, and the life-cycle stage of affected

Figure 6 — Relative Emissions of Carbon Dioxide Where Methanol Is Produced From Coal



organisms. Except in cases of large spills over extended periods, impacts are expected to be minimal.

Terrestrial Ecosystems

Bevilacqua also reported that terrestrial ecosystems affected by a methanol spill will recover within weeks because of methanol's volatility, miscibility, and biodegradability. Evidence shows that gasoline spills can cause extensive and long-term damage.

Methanol-induced narcosis in insects usually was found to be reversible (D'Eliscu 1979). Fungal and bacterial populations appeared to be tolerant to methanol spills in the soil; recovery of more than 90 percent has been observed over a 3-week period (SMFTC 1986).

Methanol's effects on vegetation can last more than 1 year, with a biomass reduction of approximately 65 percent at the end of 1 year. This reduction would be less from gasoline. The impact of methanol-gasoline blends was somewhat more severe than from gasoline alone. Methanol spills are not expected to have any greater overall effect than gasoline spills (SMFTC 1986).

HEALTH AND SAFETY ISSUES

The emission characteristics of methanol vehicles relative to those of conventional gasoline and diesel vehicles may change the risk of public exposure to pollutants if market penetration of methanol vehicles becomes significant. This includes exposure to air pollutants and liquid effluents from fuel production, as well as liquid and solid wastes from vehicle and fuel production, distribution, use, and disposal. This analysis does not attempt to quantify these changes. A preliminary literature review did not identify any major health-related problems.

The following subsections address public health and safety issues associated with the normal operation of methanol vehicles and with accidents. A comparison of the occupational safety issues associated with methanol production and distribution against those associated with petroleum production and distribution is not part of this report.

Hazards Based on Exposure to Methanol

The health risks from methanol are derived from the relative toxicity of fuel exposure by inhalation, ingestion, or dermal contact. Table 3 summarizes the available data for inhalation. Identified human illnesses include organic solvent poisoning, systemic acidosis, and effects on the central nervous system (Potts 1986). Estimated tolerance levels reported by Bevilacqua et al. (1980) are provided in Table 4. Observed lethal doses range from 15 to 255 grams (Wimer et al. 1984). The odor of gasoline in blends should prevent the accidental ingestion of those fuels.

Machiele (1987) generated a comprehensive report on the hazards of various methanol-gasoline blends and identified the hazards with blends as more serious than those of neat methanol or gasoline. Methanol in sufficient quantities tends to cause narcosis and may result in permanent neural damage and physical impairment to humans. However, short-term exposure to methanol below the threshold limit value does not constitute a major health hazard.

A recent review of methanol's health effects indicated that continued exposure to low levels of methanol may result in effects similar to those caused by acute exposure (Health Effects Institute 1987). Chronic exposure by inhalation to methanol above 200 parts per million has resulted in dizziness, headaches, nausea, and blurred vision. In general, no overt health problems are associated with low-level exposures. Table 5 provides comparative toxicity ratings for methanol, gasoline, and formaldehyde.

Fuel-System Hazards in Normal Operation

Chronic leaks or major spills from methanol fuel systems are not expected to have major irreversible effects. While the effect of methanol-gasoline blends may be somewhat stronger, as well as longer, no long-term or permanent damage is expected, according to both Bevilacqua et al. (1980) and Machiele (1987).

Table 3 — Health Hazards of Selected Fuels

Exposure Type	Gasoline	Methane	Methanol	Propane	Hydrogen
Inhalation					
Threshold limit for repeated exposure	Varies	Nontoxic	200 ppm	1,000 ppm	Nontoxic
Principal effects of exposures above threshold limit	Varies	Nontoxic (Simple Asphyxiant)	Narcosis	Narcosis	Nontoxic

Source: SMFTC (1983)

Table 4 — Estimated Tolerance Levels for Methanol (ppm)

Inhalation Exposure Duration	Tolerance Level
Single exposure	
1 hr.	1,000
8 hr.	500
24 hr.	200
40 hr.	200
168 hr.	50
30 d.	10
60 d.	5
90 d.	3
Related exposures	
1 hr./d.	500
2 hr./d. ^a	200

Note: Based on five 8-hr. working days.

^aEither two 1-hr. exposures or one 2-hr. exposure per day.

Source: Bevilacqua et al. (1980).

Fuel-System Hazards in Accidents

No documentation is available on accident statistics with methanol-fueled vehicles. However, the properties of methanol make it a far less significant risk than gasoline, although fires with methanol-gasoline blends may be more severe because of the gasoline.

Fire Hazards

In ventilated areas, the ignitability of neat methanol fuels is between those of gasoline and diesel fuel. Methanol-gasoline blends, however, tend to behave more like gasoline because of their high volatility. Neat methanol is flammable over a wide temperature range in an enclosed environment, while the high volatility of methanol blends makes them less of a fire risk in enclosed spaces.

Relative to gasoline or diesel fires, neat methanol and M85 fires are more controlled and burn cooler because of their lower combustion heats and higher vaporization heats. A major problem with methanol fires is their invisibility in daylight; one suggested solution is the addition of unleaded gasoline in volumes of at least 10 percent (Fanick et al. 1984). Machiele (1987) provides a scale that ranks the risks of various fuels. However, this ranking appears to be subjective and does not provide a comparison with gasoline or diesel fuel as baseline materials.

Table 5 — Comparative Toxicity Ratings of Gasoline, Methanol, and Formaldehyde

Substance	Eye Contact	Inhalation	Skin Penetration	Skin Irritation	Ingestion
Gasoline	(2)	(3)	(3)	(1)	(3)
Methanol	2	2	2	1	2
Formaldehyde	4	3	4	4	3

1 = mild; 5 = extreme toxicity. Parentheses indicate estimated toxicity.

Source: Sunshine (1975).

The high solubility in water of neat methanol makes water a poor extinguisher. Indeed, water tends to spread a neat-methanol fire. Desirable extinguishers include dry chemicals, CO₂, or alcohol-resistant foam concentrates. (Petroleum fires usually are extinguished with dry chemicals, CO₂, or foams.) Methanol-gasoline blends, such as M85, pose a unique firefighting problem. Water tends to separate the fire into two zones, with the gasoline fraction burning independently and providing a flame source to ignite the nearby water-alcohol phase. The standards suggested for controlling neat methanol fires are the most appropriate for M85 fires.

Existing fire-prevention codes and recommendations include maintaining storage temperature below the flammability range, ensuring that access of air to the fuel is limited, and limiting ignition sources near the fuel. The National Highway Traffic Safety Administration has established a standard for vehicle storage tanks. The corrosive properties of methanol tend to dissolve the oxide scales formed on steel tanks, exposing new metal to be corroded by water present in the methanol. Appropriate corrective measures, such as alternative tank materials or methanol-resistant paints, should be developed to prevent container failures.

REGULATORY CONSIDERATIONS

A variety of Federal, State, and local regulations affect the operation and use of methanol vehicles. Emission regulations are of particular concern.

EPA issued emission standards for 1990 and later model-year methanol vehicles in April 1989 (EPA 1989). The CO, NO_x, particulate, and smoke standards are numerically identical to those for current vehicles. Particulate and smoke emission standards, which had applied only to petroleum-fueled diesel vehicles, are now set for methanol-fueled diesel vehicles. Idle CO standards apply to all methanol-fueled light-duty trucks and heavy-duty engines.

The exhaust and evaporative HC standards for methanol vehicles are intended to limit the ozone producing potential of these vehicles to an amount no more than that of petroleum-fueled vehicles. This is accomplished by limiting the amount of organic carbon emitted by methanol vehicles. These carbon limiting standards specifically account for non-oxygenated HC compounds as well as the oxygenated HC compounds of methanol and formaldehyde. The standards vary by engine type.

Emission certification of flexible-fuel vehicles presents numerous stumbling blocks. These vehicles must comply with the standards when tested on any fuel mixture within the vehicles' design range. The use of a worst-case blend, as is required, may result in more equipment for evaporative emission control and so a higher price for the vehicle than if the worse-case blend were not required.

COMPRESSED NATURAL GAS VEHICLES

INTRODUCTION

This section discusses the environmental, health, and safety (EHS) issues related to the use of natural gas vehicles. The focus is on issues associated with the operation of vehicles in which the natural gas is stored on board in compressed form at high pressure, that is, compressed natural gas (CNG) vehicles.

EMISSIONS AND AIR QUALITY

Emissions From Spark-Ignition Engines

Several recent reports serve as guides to evaluating the comparative emissions from SI-engine vehicles fueled by CNG versus gasoline. EA-Mueller, Inc. (1988) drafted a report that addressed emissions in an overall assessment of the state of CNG vehicle technology. EPA (1988) discussed CNG vehicles in its guidance to States on incorporating alternative-fuel vehicles in the design of ozone-reduction strategies. Alson (1988) provided an even more current assessment of the emission characteristics of CNG vehicles.

Data on emissions from CNG vehicles are very limited, particularly for vehicles meeting current emission standards (that is, model year 1981 and later passenger cars and 1984 and later light-duty trucks). EA-Mueller collected available emission test results (but only from the Federal test procedure for such vehicles); the results, expressed as percentage changes in HC, CO, and NO_x emissions from baseline gasoline vehicles, are shown in Table 6 (Bechtold 1988). Emission test results of dedicated and dual-fuel CNG vehicles are combined. Essentially, Table 6 includes the results of only three to four testing programs.

A wide range of CO, NO_x, and HC results is presented in Table 6. Factors that contributed to the varying emissions data include engine tuning to obtain lower emissions of one pollutant (for example, leaning to reduce CO emis-

sions), which also alters other emissions; variation in the components of natural gas conversion kits (for example, different numbers of pressure regulators); engine and conversion kit wear; and differences in the configuration and condition of vehicle emission-control devices.

Carbon Monoxide. Despite the wide ranges shown in Table 6, CO emissions generally are much lower with natural gas than with gasoline, largely because of better air-fuel mixing and leaner combustion. The CO increase shown for light trucks occurred in one test of a 1984 dedicated CNG Ford Ranger pickup (Powrie 1985). A flexible-fuel version of the same vehicle (that is, one capable of operating on CNG or gasoline) averaged 52 percent lower CO emissions than its gasoline counterpart. EA-Mueller indicated that the dual-fuel version obviously was operating leaner than the dedicated version, but no reason was given for why the latter's CO emissions were higher. In another test of a dedicated 1984 Ford Ranger operating on CNG, CO emissions were reduced 99 percent compared with its gasoline counterpart (Adams 1985).

EPA's estimate of the relative CO emissions of natural gas vehicles is consistent with the results reported by EA-Mueller. EPA estimates a 50-percent reduction in CO emissions with CNG use (EPA 1988).

Oxides of Nitrogen. As evident from Table 6, NO_x emissions can increase or decrease with the use of natural gas. These emissions are highly dependent on spark timing and air-fuel mixture adjustments and the degree of interaction with the emission-control system (for example, whether the feedback control of the three-way catalyst is operating efficiently with natural gas).

EPA expects a 40-percent *increase* in NO_x emissions with natural gas because the majority of the data that it reviewed indicated a NO_x increase with CNG and because lean operation, a consequence of CNG use (unless

Table 6 — Comparison of Emissions From CNG-Fueled Spark-Ignition Vehicles Relative to Conventional Gasoline-Fueled Spark-Ignition Vehicles

Emission	Percentage Change	Comments
Passenger cars, post-1980		
CO	-6 to -99	Due to better mixing and lower cold-start CO emissions
NO _x	+40 to -85	Depends on whether spark timing has been adjusted and on interaction with gasoline emission-control system
HC (total)	+697 to -44	Wide variation in data
Light trucks, post-1983		
CO	+80 to -99	Depends on CNG fuel-system calibration
NO _x	+73 to -65	Depends on spark-timing compensation and emission system interaction
HC (total)	+1,071 to +200	—

Source: EA-Mueller, Inc. (1988).

the air/fuel ratio is adjusted for CNG use), causes higher emissions. The EPA NO_x estimate is the average of the range of data available to EPA (EPA 1988).

Hydrocarbons. Also evident in Table 6 is the significant increase in total HC emissions from natural gas vehicles relative to those from gasoline vehicles. This increase presumably occurs because of incomplete combustion of methane (the primary component of natural gas), flowthrough of methane when engine valves overlap, and insufficient oxidation in the catalyst. Methane is a stable component of exhaust HC emissions. In fact, in the tests represented in this comparison, total HC emissions exceeded the Federal exhaust standard—not unusual in CNG vehicles. Because EPA is concerned about the ozone-reduction potential of various alternative fuels,

it is more interested in reactivity than in total HC emissions. Its guidance document therefore focused on developing estimates of the HC-reduction potential of alternative fuels that incorporate the often lower reactivities of the various HC components of these fuels.

For example, limited data suggest that 80 percent of the HC exhaust from CNG-fueled vehicles is methane (EPA 1988). Methane is photochemically nonreactive except over long periods. EPA has thus developed estimates of HC emissions from CNG-fueled vehicles that incorporate the effect of the reduced overall reactivity of CNG components. According to EPA estimates, CNG vehicles will reduce exhaust HC emissions 40 percent (reactivity accounted for) and eliminate evaporative HC emissions. While these estimates appear to differ greatly from EA-Mueller's, actually they

do not; data available to EA-Mueller indicated high methane content in the total HC emissions of CNG vehicles.

Aldehydes. Very little test data are available on aldehyde emissions from CNG vehicles. In general, it is expected that formaldehyde emissions, a major concern with methanol, should not pose problems with CNG. One study, in which model-year 1968–70 vehicles were tested, concluded that aldehyde emissions were lower with CNG than with gasoline; however, emission-control technology has changed significantly since those model years (Fleming et al. 1973). Alson (1988) reports that emission testing showed that formaldehyde levels from CNG vehicles generally are equivalent to or lower than from gasoline vehicles. However, Alson did not stipulate the dates of the tests that are the source of this conclusion.

EPA did not estimate changes in aldehyde emissions from CNG vehicles. A change in aldehyde levels would contribute to changes in ozone precursors and should be considered specifically (as a line item) in the HC-reduction estimates.

Additional Testing Needs. Additional testing is required to more accurately depict the emissions of natural gas vehicles. In particular, the likelihood of increased oxides of nitrogen (NO_x) emissions with CNG, the proportion of HC exhaust that is methane, and the relative level of aldehyde emissions need to be evaluated. Also, the differences in emissions between dual-fuel and dedicated CNG vehicles need to be better defined. EPA has indicated that dedicated CNG vehicles are likely to achieve lower emission rates than those discussed in its 1988 guidance document, but confirming data are not available.

Emissions From Compression-Ignition Engines

Available data on exhaust emissions from natural-gas-fueled CI engines also are very limited. Most of the test results summarized in Table 7 are from fumigated CNG single- or multi-cylinder CI engines with no emission-control devices. (In fumigation, the gas enters the engine with the intake air.) Tests on CI engines converted to SI for natural gas use

and tests on engines into which natural gas is directly injected have not been reported.

As Table 7 shows, diesel vehicles converted to dual-fuel CNG-diesel operation with fumigation have four general exhaust emission traits relative to diesel only operation: increased HC emissions (although most are methane); increased CO emissions (though at high load they may be equal); decreased (but not always) particulate emissions; and equivalent or slightly lower NO_x emissions.

Hydrocarbons. HC emissions are increased in natural-gas-fueled CI engines (relative to diesel fuel), though most are methane. This increase is due to the large quench volumes in the combustion chamber (which is filled only with air during diesel-fuel operation) and to incomplete combustion because of the slow flame speed of natural gas. The HC increase is in direct proportion to the amount of unburned fuel trapped in the quench volume. Available test results do not indicate whether CNG vehicles would exceed HC emission standards for CI engines.

Carbon Monoxide. Emissions of CO increase (assuming the overall air/fuel ratio is not rich) in regions where the combustion process is extinguished, either because the temperature is too low or there is not enough time for completion of the combustion reactions (due to slow flame speed). Available test results do not indicate whether CNG vehicles would exceed CO emission standards for CI engines.

Oxides of Nitrogen. NO_x emissions, while generally considered to be the same or lower than NO_x emissions from diesel-fueled CI engines, also vary by load.

Aldehydes. Aldehyde emissions were found to be higher in CNG-fueled CI engines, but this result is based on only one study of an indirect-injection diesel engine (EA-Mueller, 1988).

Particulates. Particulate emissions generally, though not always, are expected to be lower. Natural gas burns soot- and particulate-free and is nearly sulfur-free. However, engines with high oil consumption may have a small but measurable quantity of particulate emissions. One test result shows that particulate emissions vary by engine load.

Table 7 — Summary of Exhaust Emissions From Fumigated CNG-Fueled Compression-Ignition Engines Relative to Diesel-Fueled Engines

Emission	Test Parameter	Relative to Straight Diesel Fuel
Total HC	Low load	Much higher
	High load	Slightly higher
Methane	All operating conditions	Much higher
Nonmethane	Low loads/rich mixture	Higher
	High loads/lean mixture	Equal
CO	Low load	Higher
	High load	Equal
NO _x	Low load	Lower
	High load	Equal
Aldehydes	Low load (one test)	Much higher
	Full load (one test)	Slightly higher
Formaldehyde %	All operating conditions (one test)	Much higher
Particulate mass loading rates	Low-to-medium load (one test)	Much higher
	Full load (one test)	Lower

Source: EA-Mueller, Inc. (1988).

General. Given the few available test results for natural gas use in CI engines, only a general assessment can be made of CNG's overall relative impacts on emissions. Specific assessments are unavailable in the literature reviewed. Generally, CI-powered natural gas vehicles can be designed to lower overall NO_x and particulate emissions; however, power and performance tradeoffs are unknown.

Unresolved Technical Issues Affecting Emissions

In addition to the rather sparse data on emissions, unresolved technical questions add to the uncertainty about emissions from CNG-fueled vehicles.

Effects of Improperly Installed Conversion Kits. Numerous firms produce and market kits for converting gasoline vehicles to dual-fuel operation. EPA (1988) indicated that some kits, if installed improperly, may result in increased emissions with gasoline operation and no reductions in emissions with CNG. However, data are insufficient to identify these kits.

Emissions of Dual-Fuel Vehicles Operating on Gasoline. Increased emissions from dual-fuel vehicles operating on gasoline may be a more general problem than just one of improper installation of conversion kits. For example, in one test of two model-year 1979 and 1980 dual-fuel vehicles operating on gasoline and presumably properly converted,

emissions of HC, CO, and NO_x were 5 to 30 percent higher than from the baseline gasoline vehicle (DOE 1982). In a more recent test of a dual-fuel 1984 vehicle, HC emissions from gasoline operation were 3 to 4 times higher than those from the baseline gasoline vehicle; CO emissions were 15 to 68 times higher; and NO_x emissions were considerably lower (the values presented here are estimated for urban and highway driving separately) (Powrie 1985). While these results exist, the EPA's guidance document assumes no change in emissions when operating a dual-fuel vehicle on gasoline.

Compatibility of CNG Vehicles With Present Exhaust-Emission-Control Hardware.

Present conversion kits have little or no interaction with hardware for controlling vehicle exhaust emissions (Mueller/E:F Technology 1983). Some controls (for example, exhaust gas recirculation and spark timing control) are likely to function when the vehicle operates on natural gas, although their effectiveness may be diminished.

Three-way catalysts, which oxidize CO and HC while reducing NO_x, will not be effective with an open-loop gaseous fuel system (Mueller/E:F Technology 1983). The oxidation portion of the catalyst may continue to be effective, but the NO_x-reducing portion is likely to have little or no effect on NO_x emissions. Three-way catalysts work most efficiently with a stoichiometric mixture, so that HC and CO oxidation and NO_x reduction are both effective. However, because existing CNG conversion kits have no interaction with the on-board computer systems, constant stoichiometry is not maintainable. Because CNG vehicles tend to run lean and NO_x emissions increase with lean combustion, NO_x emissions from CNG combustion will not be mitigated by current emission-control hardware.

In a related problem, many newer vehicles with on-board computer control of the three-way catalyst system (plus other emission-control hardware) and with spark timing may not operate properly with current gaseous fuel systems. One resultant problem is that gasoline flow to the engine is stopped during natural gas operation, which can result in gumming and corrosion of fuel lines and injectors. It also can cause error codes to be

stored in the computer, resulting in degraded engine operation at all times (and presumably degraded emission performance). However, research is under way to develop electronically controlled CNG fuel-metering systems that will provide more precise fuel delivery. Such systems should be well-suited to having feedback control of the air/fuel ratio, thereby allowing effective use of a three-way catalyst.

Cold Starting. Cold starting and its effect on emissions, a major concern with other fuels, should not pose problems for CNG. As a gaseous fuel, CNG has superior cold-start characteristics.

Efficiency and Performance of CNG Vehicles Relative to Emissions. The efficiency and performance of CNG vehicles are possible concerns, particularly with dual-fuel retrofits. Each of the three post-1980 dual-fuel vehicles that EPA examined suffered significant losses in efficiency or acceleration (Alson 1988). This trend is also confirmed by evaluations of pre-1981 vehicle conversions. Decreased efficiency and/or performance is especially relevant with a dual-fuel vehicle because of the potential for the user to use only gasoline or to tamper with the CNG control system—both of which likely would increase emissions. However, there is theoretical and practical evidence (based on the Ford Ranger tests) that dedicated and optimized CNG vehicles may have efficiency and performance levels at least equivalent to those of gasoline vehicles (Alson 1988).

Low-Level Ozone-Reduction Potential of CNG Vehicles. As indicated earlier, EPA projects a substantial reduction with CNG vehicles in the exhaust HC ozone-precursor emissions, largely because approximately 80 percent of the exhaust HC of CNG vehicles is nonreactive methane. However, because HC emissions from CNG vehicles often are much higher than those from gasoline vehicles, CNG vehicles can still produce a substantial volume of reactive nonmethane HC emissions—even if they account for only 20 percent of total HC emissions.

Alson (1988) analyzed the results of three test programs of post-1980 dual-fuel vehicles and two dedicated CNG vehicles and found that nonmethane HC (NMHC) emissions are not always lower with CNG vehicles. In dual-fuel

vehicles, nonmethane HC emissions during CNG operation were significantly higher in one case, equivalent in the other, and significantly lower in the third. With the dedicated CNG vehicles, NMHC emissions increased in one vehicle and decreased in another. Examination of test results of model-year 1981–83 vehicles converted by Dual Fuel Systems, Inc., confirms these variations (Seisler 1985). While EPA continues to project that future advanced-technology CNG vehicles will provide large reductions in NMHC emissions (and thus ozone precursors), it is clear that additional analysis is required to confirm this important assumption.

Additional analysis of the relative reactivities of NMHC emissions of CNG vehicles compared to those of gasoline vehicles would also be useful. EPA assumes that NMHC emissions from CNG operations have an overall reactivity similar to that of NMHC gasoline emissions (Alson 1988). Why this should be true is not clear. Gasoline combustion results in a large number of individual organic products: up to 200 HC compounds have been found, each with different smog-forming tendencies (Mueller Associates, Inc. 1985). CNG combustion presumably results in fewer NMHC compounds because it is initially a much simpler fuel. The overall reactivity of these products may differ from that of gasoline HC emissions, and this would affect calculations of CNG's ozone-reduction potential.

The ozone-reducing potential of CNG's significantly lower CO emissions also should be addressed. A recent study by Systems Applications, Inc. showed that CO also is an ozone precursor (Alcohol Update 1988); therefore, CNG's lower CO emissions could contribute to lowering ozone levels.

Implications for Urban Air Quality

Based on current data on emissions from natural gas vehicles and assuming resolution of the various unresolved technical issues described in this section, the following general conclusions can be reached on the potential effect of natural gas emissions on urban air quality (nationally and locally):

- Almost certainly, spark-ignition (SI) engines using CNG will contribute to reduced carbon monoxide (CO) levels.

- Although some tests have shown higher levels of reactive HC emissions with CNG vehicles, natural gas vehicles with SI engines probably will reduce the reactive HC's that are precursors to ozone formation. However, the overall ozone-reduction potential of these vehicles is unclear. NO_x emissions, which also are ozone precursors, are expected to increase, while CO emissions—also recognized as ozone precursors—will be much lower with CNG.
- Natural gas vehicles with compression-ignition (CI) engines will reduce ambient particulate levels in the "breathing zone" that is now significantly affected by the diesel vehicles that the CI natural gas vehicles would presumably replace.
- Although CI engines using CNG likely will increase HC and CO emissions relative to diesel fuel, the degree of increase has not been determined.

Implications for Other Air-Quality Phenomena

Urban air quality is not the only air-quality concern, however. Several other phenomena have been gaining increasing attention: global warming, stratospheric ozone depletion, and acidic deposition.

Global Warming. Because of the current concern over greenhouse gases, emissions of carbon dioxide (CO₂) and methane from natural gas vehicles should be compared with those from gasoline and diesel vehicles. Two references provide such comparisons: Mueller Associates (1987) estimated that natural gas vehicles emit 25 percent less CO₂ than do gasoline vehicles during vehicle operation, while DeLuchi et al. (1987), in a more detailed analysis, estimated that CNG vehicles would reduce emissions of greenhouse gases 19 percent relative to gasoline and diesel vehicles.

DeLuchi et al. incorporated estimates of methane, nitrous oxide, and CO₂ generation by all three vehicle types (gasoline, diesel, and CNG) and put these emissions on a CO₂-equivalent emissions basis. Further, they incorporated estimates of these emissions from fuel production, processing, and transmission, as well as vehicle operation. The

estimated reduction in CO₂-equivalent emissions with natural gas vehicles is sensitive to the value assumed for the methane-to-CO₂ conversion factor; however, even when that value was varied, natural gas vehicles never exceeded the CO₂-equivalent emissions of gasoline and diesel vehicles.

Stratospheric Ozone Depletion. Stratospheric ozone depletion may be affected by CNG vehicles in two ways. Mueller Associates (1987) suggests that NO_x can participate in a series of reactions that reduce stratospheric ozone. Given that CNG vehicles may increase NO_x emissions, their use could cause additional depletion of stratospheric ozone.

However, methane—a large component (up to 80 percent) of HC emissions from CNG (EPA 1988)—is involved in an upper atmosphere reaction that ties up the chlorine atoms released by CFC's that would otherwise react with and deplete the ozone. Methane emissions would increase with the use of CNG. Unfortunately, the tradeoffs between these two emission types and their effects on stratospheric ozone depletion is unclear. DeLuchi et al. (1987) additionally point out that there is disagreement about the extent to which ground-level ozone precursors ultimately affect stratospheric ozone concentration.

Acidic Deposition. With respect to acidic-deposition precursors, CNG vehicles may actually increase NO_x levels. Because CNG combustion produces no sulfur oxides (SO_x), these vehicles would lead to a reduction in the relatively small contribution of mobile sources to SO_x totals. The significance for acidic deposition of this tradeoff between (potentially) increased NO_x and decreased SO_x is not clear. A change in acidic deposition is not expected to be large with a relatively small number of CNG vehicles in operation.

HEALTH AND SAFETY ISSUES

This section focuses largely on concerns related to the fuel-system hazards of CNG vehicles in normal operation and in accidents. Much of the following discussion is drawn from a 1984 state-of-knowledge assessment of CNG vehicles (Singh 1984). Concerns associated with vehicle or fuel production or distribution are not discussed in this report.

Health Risks

Methane—the major component of CNG—in sufficient quantities is a simple asphyxiant (that is, it displaces air) but is otherwise nontoxic (see Table 3). In general, methane appears to have a significantly lower adverse health impact than does gasoline.

Because CNG vehicles produce different levels of NO_x, CO, HC, and particulate emissions than do gasoline or diesel vehicles, there may be changes in public exposure risk from these air pollutants. Similarly, substantial penetration of CNG vehicles would change the public's exposure to air pollutants from fuel production and to water effluents and solid wastes from vehicle and fuel production, operation, and disposal. No attempt has been made to quantify here the changes in these pollutants or the effects of these changes on public health. Based on a cursory literature review in this area, however, no major shifts in health impacts are anticipated.

Fire Hazards Based on Fuel Properties

Table 8 lists selected properties of CNG, gasoline, and diesel fuel. Density affects safety. Vapors or gases that are heavier than air tend to settle near the ground, where they can form flammable mixtures. At its normal boiling point (-259°F), methane is heavier than air, but natural gas released from CNG tanks at ambient temperatures is considerably less dense than air and will rise, diffuse, and disperse in unconfined spaces. Thus, natural gas at ambient conditions tends to be safer in unconfined areas than gasoline vapor, which is heavier than air. In confined areas, the more rapid dissipation of natural gas is a disadvantage because flammable air-fuel mixtures could accumulate more readily. However, because the flammability limit of natural gas is greater than 5 percent, considerably more fuel (relative to gasoline) must mix with the air to render the mixture combustible. Furthermore, the fire hazard would persist longer with gasoline.

A lower flammability limit is one criterion for evaluating relative fire hazards, especially for small leaks or spills. Methane's flammability limit is higher than gasoline's, which indicates a lower fire hazard for CNG. In addition, methane's higher autoignition temperature (the

Table 8 — Selected Properties of CNG, Gasoline, and No. 2 Diesel Fuel

Property	Compressed Natural Gas ^a	Gasoline	No. 2 Diesel Fuel
Flammability limits (vol. % in air)	5.3–15.0	1.0–7.6	0.5–4.1
Detonability limits (vol. % in air)	6.3–13.5	1.1–3.3	—
Minimum ignition energy in air (mJ)	0.29	0.24	0.3 (est.)
Autoignition temperature (°F)	1,004	442–880	500
Flash point (°F)	Gas	-45	min. 125
Energy content (lower heating value) Btu/gal.	19,760 ^b	116,400 ^c	129,400 ^c
Btu/lb.	21,300	18,900 ^c	18,310 ^c
Diffusion coefficient in air ^c (cm/sec.)	0.16	0.05	—
Buoyant velocity in air ^d (m/sec.)	0.8–6	Non-buoyant	Non-buoyant
Density of liquid (g/cm ³)	—	0.70–0.78 ^e	0.82–0.86
Density of gas relative to air (air = 1.00)	0.555	3.4	>4.0 (est.)
Vapor pressure ^f (atm)	1	0.6–0.8	0.0005
Normal boiling point (°F)	—	100–400	405–620
Storage conditions	Compressed gas at 2,400–3,000 lb/in. ² (gage)	Liquid at ambient temp. and pressure	Liquid at ambient temp. and pressure

^aProperties are primarily those of methane. Because natural gas sources vary in composition, values will deviate to a small extent from those of pure methane.

^b2,400 lb/in.² and 70°F.

^cAverage value.

^dAt normal temperature and pressure.

^eAt 1 atmosphere (atm).

^fFor gaseous fuels, this is "equivalent vapor pressure" when released from high-pressure storage container or the maximum possible pressure in ambient environment. For liquid fuels, it is the value of the vapor pressure at maximum ambient temperature.

Source: Singh (1984).

lowest temperature at which a combustible mixture of fuel and air can ignite in the absence of an external ignition source) compared to gasoline also makes CNG less of a fire hazard than gasoline. However, only small amounts of energy from relatively weak ignition sources are required for ignition of methane. Spark-ignition energy, or minimum ignition in air, is essentially equivalent among the various fuels listed in Table 8.

Flash point, the lowest temperature at which an ignitable vapor-air mixture will occur above the liquid surface, is another important safety property of liquid fuels. Methane flames are clean burning, yellowish, and visible in daylight, but they are not as easily seen as gasoline flames, which are similar to those of methane but are mixed with soot and smoke, making a fire obvious. Under the identification system for flammability hazards established by the National Fire Protection Association (NFPA), gasoline is rated at 3, whereas methane is assigned a rating of 4, the most severe hazard.

Considerable uncertainty surrounds the question of whether methane-air mixtures can detonate in unconfined conditions. Detonations of unconfined methane-air mixtures at ambient conditions have been observed experimentally, but only when initiated by more than 1 kilogram of high explosives. Nonetheless, a bursting cylinder or tank could generate a shock wave strong enough to cause detonation. Furthermore, very small amounts of ethane—a constituent of natural gas—enhance the detonability of methane-air mixtures.

Detonations of confined methane-air mixtures have been produced experimentally by explosive charges weighing much less than 1 kilogram. Accidental explosions of natural gas in sewers and tunnels have been documented. Presumably, these were initiated by weak thermal ignition sources, such as open flames, hot surfaces, or sparks.

Based on an examination of physiochemical properties, Los Alamos National Laboratory derived preliminary rankings of the relative safety of natural gas, gasoline, diesel fuel, and liquefied petroleum gas (LPG) (Krupka et al. 1983). Fuels were ranked according to specific properties in isolation and in combination with each other. On the basis of these preliminary

rankings alone, Los Alamos concluded that it is difficult to designate any one fuel as significantly safer than another.

Fuel System Hazards in Normal Operation

Fuel Leakage. Fuel release is the principal concern in normal operation because it can lead to an accumulation (in a vehicle compartment or storage area) of a combustible mixture. Fuel can be released by spills or leaks during vehicle fueling or through fuel-system malfunctions. Leaks can occur throughout the system, and normal operation of pressure-relief devices can also release fuel.

Overall, leakage potential can sometimes be greater in gaseous fuel systems than in liquid systems because of higher storage pressures and lower molecular weights and viscosities. Furthermore, the complexity of dual-fuel systems may provide more potential leakage paths than would a liquid or gaseous single-fuel system. However, in the case of nontoxic methane, release of small amounts of fuel is not hazardous, provided the gas is dispersed before its concentration reaches the lower flammability limit of 5 percent. The hazards associated with gas release by leakage from fittings appear to be controllable via existing technologies and established procedures (for example, inspection and maintenance; fuel system isolation from the passenger compartment; venting of the passenger compartment, trunk, and engine area; and use of gas-sensing devices or odorants) (Singh 1984).

Corrosive Failure of CNG Cylinders. Tank corrosion is a safety concern in CNG vehicles. In the past, corrosive constituents of natural gas, such as hydrogen sulfide (H_2S), have caused catastrophic failure of steel cylinders used for bulk transport and storage. The U.S. Department of Transportation (DOT) currently prohibits the transport of natural gas in cylinders with a volume greater than 1,000 gallons. Special tube trailers are permitted as an exemption to DOT regulations, but allowable levels of H_2S and hydrogen are lower than those for pipeline-quality gas from gas-distribution systems (water is a key contaminant because neither H_2S nor other contaminants can produce significant amounts of corrosion in the absence of moisture) (EA-Mueller 1988).

Cylinders in CNG-powered vehicles are not subject to DOT regulations, and no Federal fuel quality standards exist for natural gas as a vehicle fuel. Because of this and the potential for hazardous conditions, the NFPA in 1984 adopted a CNG Vehicular Fuels Systems Standard NFPA52 (NFPA 1984). This standard required that cylinders be manufactured, inspected, and tested in accordance with DOT regulations and exemptions for commercial cylinders and that gas quality be such that water vapor essentially cannot condense. (By limiting water content, other contaminants should not be of major concern.)

However, DOT has pointed out that vehicle operating conditions may be more difficult (for example, CNG is more likely to have contaminants and the pressures are likely to be higher) than those in normal commercial applications (U.S. Department of Transportation 1985). These more severe operating and environmental conditions may cause abnormal cylinder deterioration, and DOT therefore concluded that it cannot ensure the adequacy of cylinders built to DOT specifications for CNG vehicle fuel-system use.

DOT's concern applies to all cylinders, including those of aluminum or composite materials. However, one study concluded that composite cylinders are more likely to crack in their inner shells. The gas would then flow through the crack and pass through the outer reinforcement, which would not contain the gas. This type of controlled release is a much lower hazard than is the bursting of a steel cylinder (Singh 1984). EA-Mueller (1988) also reported that, in a number of tests, neither hydrogen sulfide nor other contaminants were found to be corrosive to aluminum alloys. Some relatively inexpensive means of in-use cylinder testing to detect inner-shell cracks may be needed as CNG vehicles are commercialized. Recent success with acoustic detection, which can be performed during vehicle refueling, has been reported in Canada (Carter 1987).

Fuel-System Hazards in Accidents

Control of Fuel Release on Impact. Accidents that puncture or crush the fuel tank or damage other parts of the fuel system can cause fuel releases; however, steel cylinders designed to meet DOT standards are quite rugged compared with the conventional gaso-

line tank. Several test programs have demonstrated this ruggedness—no fuel was released in 50-mile-per-hour rear-end collisions or in drop tests (Singh 1984). Lightweight CNG tanks developed in the early 1980's might be more vulnerable to collision damage and subsequent fuel leakage and fire, though their integrity in accidents has not been thoroughly evaluated (Singh 1984). Release from high-pressure lines also is possible in an accident; however, there are automatic shutoff valves and excess-flow devices to prevent such releases.

Control of Fuel Tank Rupture in Fires.

Overpressure due to fire can release fuel, cause the fuel tank to explode, and damage persons and property. One approach to controlling fuel-tank rupture in a fire is the use of pressure-relief devices that allow controlled fuel release. This approach is embodied in the DOT regulations for transport cylinders. However, DOT has indicated that a relief device system based on these requirements may not be adequate to prevent rupture of a partially charged cylinder in a fire because of the longer time required for pressure to increase to the level needed to activate the relief device. This longer exposure to fire could weaken the cylinder and cause failure before the relief device activates (U.S. Department of Transportation 1985).

Control of Passenger Compartment

Intrusion. Passengers can be injured if fuel-system components intrude into the passenger compartment. Such intrusion can be caused by failure of the cylinder-retention system due to impact deceleration forces or by insufficient available crush distance (that is, the distance between the rear bumper and the fuel cylinders) in a rear-end impact. DOT has reported two instances of retention-system failure, one of which resulted in passenger compartment intrusion (Singh 1984). If tanks can be mounted under the vehicle it will be easier to design the retention system to prevent passenger compartment intrusion.

Dual-Fuel Systems Hazards.

Current dual-fuel systems are installed as after-market kits. They are therefore not integrated into the original vehicle's safety design and testing and are not subject to DOT crash standards. For example, when the heavy steel cylinders are installed in an intermediate or compact car, the

shift in weight distribution alters the vehicle's handling characteristics. However, this problem can be mitigated to some extent by strengthening the suspension (Singh 1984).

In dual-fuel systems, fire from release of one fuel can cause damage, fire, or explosion in the other fuel system. Moreover, release of both fuels can broaden the flammability range associated with either fuel individually. In one study, 5 to 10 gasoline fires occurred in dual-fuel vehicles because of gasoline leaks attributable to faulty installation of gasoline bypass piping. During some of these fires, the natural gas ignited and contributed to the severity of the fire. An improved gas venting system was installed to remedy this problem.

Hazards In Vehicle Refueling. CNG refueling involves the danger of igniting the small amount of vapor released when the fill hose is disconnected. The filling manifold in the fueling station consists of fill-vent valves, flexible hoses, and fittings that allow the operator to fuel the vehicle. When the fill-vent valve is closed after vehicle filling, the gas in the hose is vented about 10 to 12 feet above the ground. One report concluded that, with attention to proper procedure, CNG refueling was no more dangerous than gasoline refueling (Singh 1984). Gasoline refueling itself involves the danger of igniting the vapor-air mixture and any spilled liquid.

Although it is standard practice to interlock the vehicle ignition with the fueling system so the engine cannot be started while it is being fueled, a vehicle could still roll away while connected to the filling manifold, thereby releasing fuel.

Safety History of Natural Gas Vehicles

Detailed accident data for CNG vehicles are sparse. An overall assessment of the available accident data suggests, on a rigid statistical basis, that the low number of fire and explosion accidents encountered to date may be statistically minor or insignificant (Krupka et al. 1983). Furthermore, CNG vehicles are operated almost exclusively in fleets, which typically have well-trained operators and good maintenance practices and recordkeeping. Thus, statistics derived from fleet operation may not be applicable in the future to public operation of CNG vehicles.

Public Safety Summary

The safety of CNG vehicle systems remains an important issue that has not yet been completely resolved. Los Alamos National Laboratory concluded that gaseous fuels have higher relative risks in some cases but are generally as safe as—and perhaps safer than—gasoline in other cases (Krupka et al. 1983). Other studies have concluded that nothing appears to preclude the safe use of natural gas in vehicles. However, no documented, comprehensive data set has yet been developed to allow a thorough evaluation of the crash-worthiness and system integrity of CNG vehicles.

REGULATORY CONSIDERATIONS

A variety of Federal, State, and local regulations affect the operation and use of CNG vehicles. Regulations for exhaust emissions and safety are of particular concern when considering the potential for increased use of CNG vehicles.

Emission Regulations

Vehicles converted to CNG operation are subject to the antitampering provisions of the Federal Clean Air Act. However, the written antitampering policy and the actual practices of EPA in regard to conversions are not always in agreement; the result has been confusion among marketers of conversion equipment. Written EPA policy indicates that conversions be subject to the comprehensive Federal Test Procedure (FTP) or that converters obtain State or local environmental control agency approval (which is applicable only to the geographic area over which the agency has authority). California is the only State known to have an emissions-approval program for CNG vehicles. In actual practice, EPA has accepted California approval nationwide and also has recommended an alternative test procedure that is less rigorous than the FTP. However, the vehicle converter—if following the latter approach—cannot obtain EPA approval or certification that the vehicle meets EPA requirements and does not violate Federal antitampering law.

Some natural gas vehicle conversions do not meet the Federal standard for total HC emissions for light-duty vehicles, though they appear to emit lower levels of NMHC emissions than do gasoline vehicles. The HC standard was intended primarily to control ozone formation in the lower atmosphere. California grants approvals to conversions on the basis of NMHC emissions rather than on total HC emissions.

Original-equipment-manufactured (OEM) natural gas vehicles (whether dual-fuel or dedicated) presumably will be expected to meet national mobile-source emission standards when marketed. National standards currently apply to gasoline, diesel, and methanol vehicles. Similar standards will be needed for natural gas vehicles to foster their commercialization.

Safety Regulations

The Materials Transportation Bureau (MTB) within DOT establishes regulations for the design and testing of cylinders. These regulations apply to vehicles transporting bulk industrial gas. However, in practice, steel cylinders designed to meet MTB specifications are widely used in CNG vehicles. No other Federal regulations specifically address natural gas as a motor vehicle fuel.

State and local regulations applicable to natural gas used as a vehicle fuel typically are set forth in fire codes and are enforced by local fire-prevention officials. In the past, many local regulations relating to vehicle refueling systems and the installation of conversion kits were inappropriate and complex (Singh 1984). The passage several years ago of NFPA 52, which serves as a model for State and local fire code regulations, should do much, where adopted, to correct the earlier local regulations (NFPA 52 1984). However, restrictions on the use of CNG vehicles in confined areas are not addressed by NFPA 52 and continue to be a concern.

Prohibitions against CNG vehicle use on specific roadways (for example, the Baltimore Harbor Tunnel, the Eisenhower Tunnel in Colorado, and tunnels and bridges regulated by the Port Authority of New York and New Jersey) and on various other thoroughfares remain in place, though in some cases they are being reconsidered. Further, in some areas, natural gas vehicles may not use enclosed parking garages (EA-Mueller 1988). While this has not been an issue for fleets, which generally park their vehicles outside, it could develop into an issue for CNG vehicles for personal use.

ELECTRIC VEHICLES

INTRODUCTION

This section examines possible environmental effects resulting from the proposed use of electric and hybrid vehicles. Although most observers believe that substituting such vehicles for conventional gasoline-fueled vehicles will result in an overall environmental benefit, the individual batteries could create health, safety, and other problems.

EMISSIONS AND AIR QUALITY

Compared with vehicles powered by the in-vehicle combustion of various fuels, electric vehicles have two major benefits. The first is that emissions from onboard combustion of fuels are eliminated from street level, where large numbers of people breathe, with the removal of carbon monoxide (CO) probably being the most significant advantage.

The second benefit occurs when offpeak electricity generation for recharging electric vehicle batteries takes place at powerplants that produce relatively lower emissions than conventional vehicles on a per-mile basis. However, this benefit depends on the type of off-peak power production used. Use of nuclear, wind, hydropower, or stored solar power would virtually eliminate air pollution related to vehicles. Alternatively, if charging power is produced at poorly controlled powerplants that burn fossil fuels, the pollutant concentration in the area of the utility may increase significantly.

In a recent report, Hamilton (1988) estimated that, by the year 2000, 1.4 million electric and hybrid vehicles will be used in households and 2.2 million will be used commercially. He further reported that the average daily travel for these vehicles would be 33.1 miles per vehicle, resulting in a daily recharge energy requirement of 24.3 kilowatt-hours per vehicle. This corresponds to an additional nationwide electricity demand of 85.1 gigawatt-hours each weekday—equal to about 0.5 percent of the Nation's electricity demand.

Hamilton estimated that the primary energy sources would vary, with nuclear providing 3.5 percent, coal 73.9 percent, and oil and gas 14.2 percent of the additional demand. Actual distribution in 2010, however, will be highly dependent on many factors, including regional variations. It is therefore not now appropriate to estimate possible emissions caused by the additional daily demand of 85.1 gigawatt-hours; one may surmise, however, that the additional impact on the environment (and, consequently, on human health) produced by point sources of electricity generation should be a very small portion (0.5 to 1.0 percent) of the total impact.

Deluchi, Wang, and Sperling (1989) estimated the changes in transportation-related emissions that would result from substituting electric vehicles for conventional vehicles in Southern California's South Coast Air Basin. Using clearly defined assumptions for the mix of conventional and electric vehicles in 2010, with a corresponding mix of powerplants, they estimated pollutant changes as follows: hydrocarbons (HC's), reduced by 98.9 percent; CO, reduced by 98.7 percent; oxides of nitrogen (NO_x), reduced by 60.9 percent; sulfur oxides (SO_x), increased by 495.8 percent; and particulates, increased by 570.5 percent.

The increased SO_x and particulate levels would occur because coal plants are expected to provide baseload electricity in much of the South Coast Air Basin. Alternatively, where the baseload power is primarily nuclear (such as in the Chicago metropolitan area), NO_x would show a larger decrease, SO_x would change only slightly, and particulates would decline.

DeLuchi et al. (1987) also developed a composite measure of greenhouse gases using weighted concentrations for each type of gas. On a per-mile basis, the percentage changes in greenhouse gas emissions estimated for electric vehicles relative to conventional vehicles are as follows: nonfossil powerplants, reduced by 100 percent; new natural gas plants, reduced by 18 percent; 1985 South

Coast powerplant mix, reduced by 1 percent; and new coal plants, increased by 26 percent.

HEALTH AND SAFETY ISSUES

Three types of batteries have been considered for use in electric vehicles: lead-acid, nickel-iron (Ni-Fe), and sodium-sulfur (Na-S).

Lead-acid battery cells consist of positive and negative electrodes immersed in an electrolyte solution of sulfuric acid. When the system is fully charged, the active material of the positive electrode is lead dioxide (PbO_2), and that of the negative is lead (Pb). As the battery discharges, both electrodes gradually are converted to lead sulfate (PbSO_4). The overall cell reaction is $\text{Pb} + \text{PbO}_2 + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O}$. During the reaction, the electrodes remain solid because lead, lead dioxide, and lead sulfate are all relatively insoluble in sulfuric acid. The reaction is reversible, so the cell can be recharged to its initial state.

The active materials in Ni-Fe batteries are finely divided hydrated nickel peroxide (NiO_2H) for the positive electrode and finely divided iron (Fe) for the negative. The overall chemical reaction is $\text{Fe} + 2\text{NiO}_2\text{H} + 2\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_2 + 2\text{Ni(OH)}_2$. This battery may be recharged to its original condition. The Ni-Fe battery is clearly superior to the lead-acid battery in performance and life, but is relatively expensive.

The essential feature of Na-S batteries is the solid electrolyte of beta alumina, which is chemically stable with both sodium and sulfur at the operating temperature of 300 to 400°C. The active materials, sodium and sulfur, are both liquid at this temperature, and the solid electrolyte serves as the separator. To avoid precipitation of solids, the discharge normally is terminated when the positive electrode composition reaches Na_2S_3 . Na-S batteries are thus based on the discharge reaction $2\text{Na} + 3\text{S} \rightarrow \text{Na}_2\text{S}_3$.

The three batteries have very different health and safety issues. Safety problems are minimal for the lead-acid battery, with public and occupational health issues related to lead exposures the principal concern. Concern over lead toxicity has escalated because of

recent studies showing serious learning and behavior problems in children exposed to low levels of lead. It appears that a significant number of persons have disorders of metal metabolism that make them especially sensitive to even low levels of lead exposure.

In contrast, health issues are minimal for Na-S batteries; the main focus is on public safety, especially avoiding runaway sodium reactions or explosions during vehicle operation. The Ni-Fe battery presents significantly lower health and safety hazards than lead-acid or Na-S batteries; the main concern is the safe handling of hydrogen evolved during battery charging. Battery-specific health and safety issues associated with electric and hybrid vehicles are described in the following sections.

Battery Manufacturing

Lead-Acid. Approximately 80 million conventional automotive lead-acid batteries were produced in 1987. Production costs have been adversely affected by increasingly stringent Occupational Safety and Health Administration (OSHA) and Environmental Protection Agency (EPA) regulations. The impacts of a rapidly growing electric-vehicle fleet on air, water, and solid emissions from battery manufacturing plants was estimated in a previous report (Sharma et al. 1980).

Plant and near-field exposures to lead during the production of lead-acid batteries were greatly reduced after OSHA promulgated the 1978 OSHA Comprehensive Standard for Occupational Exposure to Lead, which reduced permissible air levels from 200 to 50 micrograms per cubic meter ($\mu\text{g}/\text{m}^3$) and blood levels to 59 micrograms per deciliter ($\mu\text{g}/\text{dL}$). In addition, EPA's "National Ambient Air Quality Standard for Lead" was reduced to $1.5 \mu\text{g}/\text{m}^3$ in 1978. OSHA and EPA are considering a further tightening of these standards, which could escalate the cost of lead-acid battery production.

Nickel-Iron. The manufacturing process for advanced Ni-Fe batteries is rapidly evolving. However, examination of the basic manufacturing requirements suggests that the principal emissions are those associated with airborne dust from mechanical operations, vapor from high-temperature sintering, and wastewater

effluent. A previous report has estimated the magnitude of these emissions based on specific assumptions for in-plant air and water cleanup efficiencies (Sharma et al. 1980). The hazards are clearly less serious than those associated with lead-acid battery manufacturing.

Sodium-Sulfur. The production of Na-S batteries requires high-temperature sintering of beta-alumina electrolytes, fabrication of cell and battery components, loading of reagent sodium into wick structures, loading of sulfur into porous anodes, assembling and sealing of cells, and assembling of batteries. The principal health and safety issues relate to sodium safety, especially prevention of sodium fires, sodium-water explosions, and runaway sodium-sulfur reactions. Serious accidents and explosions have been reported at several Na-S research facilities, and similar incidents are not uncommon in sodium-processing facilities.

In assembled cells, sodium and sulfur (which react violently in direct contact) are separated only by the fragile tubes of beta alumina. Propagation of failure mechanisms, in which a single cell failure results in failure of adjacent cells, has been reported. Clever cell designs that limit the amount of sodium available for reaction, together with battery designs that minimize failure propagation, have greatly reduced the likelihood of such accidents in quality-control testing and vehicle operation.

Problems related to toxic exposures and effluents are poorly known, but appear to be far fewer than those associated with lead-acid batteries.

Potential Hazards During Electric Vehicle Operation

Lead-Acid. Release of the poisonous gases arsine and stibine, hydrogen explosions during improper charging, sulfuric acid burns, and electric shock are all operational hazards related to the use of lead-acid batteries; however, none of these is difficult to overcome. The first three hazards have been greatly reduced in recent years by the widespread commercialization of sealed lead-acid batteries. However, the present tubular lead-acid batteries used in electric vehicles are not

sealed because of high accelerative power requirements; thus, potentially dangerous amounts of arsine, stibine, and hydrogen could evolve during charge. However, special cell and battery designs, charging procedures, and ventilation provisions can reduce these hazards to acceptable levels. Most observers believe that providing sufficient ventilation to reduce the chance of hydrogen explosions also will eliminate arsine and stibine toxicity hazards.

Electrical hazards could be significant in a high-voltage electric vehicle system, although isolation transformers, fuses, and other electrical safety measures can effectively deal with the problem.

Nickel-Iron. Ni-Fe batteries are essentially emission-free in normal operation. Ni-Fe batteries appear to be quite safe under normal operating conditions and are relatively resistant to accident hazards; the principal concern appears to be improper charging in improperly ventilated areas, which could result in explosion and serious injury. During recharge, however, copious amounts of hydrogen (approximately two to three times that emitted by lead-acid batteries) are released. This problem is uniquely serious in Ni-Fe batteries because the voltages for hydrogen evolution and iron reduction from $\text{Fe}(\text{OH})_2$ are similar. A number of additives and design features, including gas recombination systems, have been proposed to minimize hydrogen management problems; however, the principal safety approach appears to be providing adequate ventilation during charge.

Sodium-Sulfur. The operational safety of the Na-S battery has been actively debated since the battery's invention in 1964. There has been very little on-the-road experience with Na-S vehicles, and there is no basis for projecting accident rates. Although recent advances in cell and battery design have greatly minimized the probability of dangerous sodium reactions under normal operation, the ability of well-engineered Na-S batteries to withstand minor accidents without serious sodium reactions—a major concern—is unknown.

Serious questions remain about the safety of vehicle occupants and others during accidents or abnormal battery operation. There are

three major concerns: sodium fires, sodium-water explosions, and runaway sodium-sulfur reactions.

A "worst-case scenario" is rupture of a fully charged battery on a busy city street, perhaps after a major rainstorm. Sodium-sulfur developers have stated that this safety problem is similar in magnitude to sudden ignition of gasoline in a conventional automobile.

Battery Recycling and Disposal

Lead-Acid. For many years, lead-acid batteries were effectively recycled in the United States, and more than 90 percent of the lead was recovered for reuse. Since 1981, however, the declining commodity price for lead and the increased costs of meeting OSHA and EPA regulations and standards have greatly slowed the lead-recycling industry. The number of lead smelters dropped from 60 to 22, and the battery recycling rate declined from 94 percent in 1980 to 65 percent in 1985. Beginning in 1986, lead prices have more than doubled to their present level of about 42 cents per pound, causing battery recycling to improve from 66 percent to about 78 percent—still well below the 1980 level.

Two battery disposal routes must be considered in any analysis of environmental hazards: battery collection, reprocessing, and recycling and the uncontrolled and unregulated disposal of large numbers of discarded batteries at thousands of sites throughout the Nation. In 1988, an estimated 15 million lead-acid batteries (corresponding to 144 million pounds of lead) were "lost" to the environment through random discarding of batteries.

Batteries that enter the reprocessing scheme are melted, after which the solids are removed and the sulfuric acid is neutralized. Everything in the battery is recycled, with three exceptions: neutralized acid is safely disposed in the sewer; residual slag (less than 1 percent lead) is sent to a landfill; and hard rubber (found in only 8 percent of scrapped batteries) also is sent to a landfill. More than 99 percent of reprocessed lead is recovered for reuse.

Landfill requirements are the principal barriers to future lead-acid battery recycling. EPA has announced its intention to mandate a "Toxic Characteristic Leaching Procedure" (TCLP), in

which each load of slag is given an acetic-acid leach test. If the leach solution contains too much lead, the slag must be placed, at great expense, in a hazardous waste landfill. There are four components to this cost: hazardous waste transportation, hazardous waste landfill fees, Federal taxes, and State taxes.

Currently, almost none of the discarded slag from U.S. smelters can pass the proposed TCLP test, and thus it would require disposal in a hazardous waste landfill. The State of California already has mandated the TCLP criteria, and several California smelters apparently are on the verge of bankruptcy. Moreover, Superfund laws assign liability to scrap dealers if the smelter becomes bankrupt and must itself be safely disposed of. No insurance is now available for this contingency.

Lead-acid batteries from electric vehicles are expected to be recycled with higher efficiency than are the less valuable conventional automotive batteries. However, the large number of lead-acid batteries projected by Hamilton could result in uncontrolled random disposal of millions of pounds of toxic and acidic materials in thousands of landfills (Hamilton 1988). On the positive side, the TCLP requirements will result in greatly reduced emissions from collected and reprocessed batteries. However, there is no reliable basis for estimating the fraction of batteries that will be collected and reprocessed.

Nickel-Iron. It is reasonable to assume that nearly 100 percent of spent Ni-Fe batteries will be collected to recover the valuable nickel. Whereas the iron electrode plates probably will be discarded, the nickel plates can easily be processed for recovery of more than 99 percent of the nickel. In one scheme, the nickel electrodes are dissolved in sulfuric acid and recycled to produce nickel-active material for electrodes. Nickel producers, however, have stated that the recovered nickel is more likely to be used in making stainless steel.

The high value of the nickel in spent Ni-Fe batteries enables secondary processors to meet increasingly stringent OSHA and EPA standards without serious economic distress. Recycling of sludges from hydrometallurgical processes and advanced wastewater treatment systems is expected to effectively reduce emissions from nickel reprocessing plants. A

previous study found the health and safety effects of Ni-Fe battery reprocessing to be relatively minor (Sharr et al. 1980).

Sodium-Sulfur. The relatively low value of materials in spent Na-S batteries suggests that these batteries will be discarded rather than reprocessed. Consequently, they must be "decommissioned" or "neutralized" after use to prevent sodium-related hazards. The standard procedure will probably have three steps: total discharging of the battery to minimize the elemental sodium present; remote crushing of the battery and reaction of unreacted sodium

or sulfur; and landfill disposal. Spent Na-S batteries will require special handling to ensure safety until the sodium has been completely reacted.

Disposal of Na-S batteries represents a cost rather than a recycling credit. Consequently, there is an economic incentive for the illicit and unsafe dumping of these batteries. It may be necessary to mandate a battery "deposit" from the purchaser, to be refunded when the spent battery is returned for neutralization and disposal.

REFERENCES

Adams, T.G., *The Development of Ford's Natural Gas Powered Ranger*, SAE Technical Paper No. 852277, Society of Automotive Engineers, Warrendale, Penn. (1985).

Alcohol Update, *Alcohol Update Interview with Dr. Gary Whitten*, Ozone Study Director (May 16, 1988).

Alson, J.A., and T. Baines, *Emissions and Energy Efficiency Characteristics of Methanol Fueled Engines and Vehicles*, Nonpetroleum Vehicular Fuels III, Symposium Papers, presented Oct. 12-14, 1982, Arlington, Va., Institute of Gas Technology, Chicago, pp. 399-431.

Alson, J.A., *The Emission Characteristics of Methanol and Compressed Natural Gas in Light Vehicles*, presented at 81st Annual Meeting and Exhibition of the Air Pollution Control Assn., Dallas (June 1988).

Bevilacqua, O.M., et al., *An Environmental Assessment of the Use of Alcohol Fuels in Highway Vehicles*, Argonne National Laboratory Report ANL/CNSV-14 (Dec. 1980).

Carter, S.A., *Research of Acoustic Emissions in Natural Gas Vehicle Storage Cylinders*, prepared by CNG Fuel Systems, Ltd., for Transport Canada, publication No. TP9470E, Ottawa, Ont. (Oct. 1987).

Carter, W.P.L., et al., *Effects of Methanol Fuel Substitution on Multi-Day Air Pollution Episodes*, Statewide Air Pollution Research Center, University of California at Riverside, under contract to California Air Resource Board, ARB-86:meth86 (1986).

D'Eliscu, P.N., *Biological Effects of Methanol Spills into Marine, Estuarine, and Freshwater Habitats*, presented at International Symposium on Alcohol Fuels Technology, Methanol and Ethanol, Wolfsburg, West Germany (Nov. 21-23, 1977).

D'Eliscu, P.N., *Environmental Consequences of Methanol Spills and Methanol Fuel Emissions on Terrestrial and Freshwater Organisms*, presented at International Energy Agency's 3rd International Symp. on Alcohol Fuels Technology, Asilomar, Calif. (May 29-31, 1979).

DeLuchi, M.A., R.A. Johnston, and D. Sperling, *Transportation Fuels and the Greenhouse Effect*, Transportation Research Record 1175, Transportation Research Board, Washington, D.C. (1989).

DeLuchi, M.A., Q. Wang, and D. Sperling, *Electric Vehicles: Performance, Life-Cycle Cost, Emissions and Recharging Requirements*, Transportation Research A (in press, 1989).

Dept. of Energy, *Assessment of Methane-Related Fuels for Automotive Fleet Vehicles (Appendices)*, prepared by Aerospace Corp., Report No. DOE/CE/50179-1 (Feb. 1982).

Dept. of Transportation, *DOT Cylinders Used for Equipment and Vehicle Fuel Systems*, U.S. Dept. of Transportation, Transportation Bureau, Notice 85-5, 50-FR-41287 (Oct. 9, 1985).

Duggal, V.C., and A. Welch, *L10 Methanol Engine with Avocet—An Update*, Fourth Windsor Workshop, Alternate Fuels, sponsored by Energy, Mines, and Resources Canada and the U.S. Department of Energy, Windsor, Ontario (June 20-22, 1988).

EA-Mueller, Inc., *Gaseous Fuel Vehicle Technology State of the Art Report* (draft), Baltimore (June 1988).

Ecklund, E.E., et al., *Alcohol Fuel Use in Diesel Transportation Vehicles*, Nonpetroleum Vehicular Fuels III, Symposium Papers, presented Oct. 12-14, 1982, Arlington, Va., Institute of Gas Technology, Chicago, pp. 261-313.

EPA, *Air Quality Benefits of Alternate Fuels*, U.S. Environmental Protection Agency, Office of Mobile Sources, prepared for the Alternative Fuels Working Group of the President's Task Force on Regulatory Relief (July 1987).

EPA, *Guidance on Estimating Motor Vehicle Emission Reductions from the Use of Alternative Fuels and Fuel Blends*, U.S. Environmental Protection Agency Report EPA-AA-TSS-PA-87-4 (Jan. 1988).

EPA, *Standards for Emissions from Methanol-Fueled Motor Vehicles and Motor Vehicle Engines (Final Rule)*, 54-FR-14428 (April 11, 1989).

Fanick, R.E., et al., *Safety-Related Additives for Methanol Fuels*, SAE Paper 841378 presented at the Fuels and Lubricants Meeting and Exposition, Baltimore (Oct. 6-11, 1984).

Fleming, R.D., et al., *Natural Gas as an Automotive Fuel, An Experimental Study*, U.S. Bureau of Mines Report of Investigations No. 7806 (1973).

Francis, W., and M.C. Peters, *Fuels and Fuel Technology, A Summarized Manual*, Pergamon Press Ltd., Oxford, England (1980).

Gabele, P.A., et al., *Characterization of Emissions from Vehicles Using Methanol and Methanol-Gasoline Blended Fuels*, J. Air Pollution Control Assn., 35:1168-1175 (1985).

Gopalakrishnan, K.V., and V. Balasubramanian, *Alcohols as Diesel Engine Fuels*, Nonpetroleum Vehicular Fuels III, Symposium Papers, presented Oct. 12-14, 1982, Arlington, Va., Institute of Gas Technology, Chicago, pp. 239-260.

Hamilton, W., *Electric and Hybrid Vehicles* (Draft), Santa Barbara, CA (May 1988).

Hardenberg, H.O., *Comparative Study of Heavy-Duty Engine Operations with Diesel Fuel and Ignition-Improved Methanol*, presented at International Fuels and Lubricants Meeting and Exposition, Toronto, SAE Paper No. 872093 (Nov. 1987).

Hardenberg, H.O., et al., *Mechanical Problems with the Use of Ignition-Improved Methanol in a Heavy-Duty Diesel Engine*, presented at International Fuels and Lubricants Meeting and Exposition, Toronto, SAE Paper No. 872092 (Nov. 1987).

Harris, J.N., and A. Russell, *Air Quality Implications of Methanol Fuel Utilization*, SAE Paper No. 881198, Future Transportation Technology Conference and Exposition, San Francisco (Aug. 8-11, 1988).

Health Effects Institute, *Automotive Methanol Vapors and Human Health: An Evaluation of Existing Scientific Information and Issues for Future Research*, Health Effects Institute, Cambridge, Mass. (May 1987).

Ito, K., et al., *Methyl Nitrite Formation in Exhaust Gases Emitted from a Methanol Fueled SI Engine*, presented at the International Energy Agency's 5th International Symposium on Alcohol Fuels Technology, Auckland, New Zealand (May 13-18, 1982).

Jet Propulsion Laboratory, *California Methanol Assessment*, Pasadena, Calif. (1983).

Krupka, M.C., et al., *Gaseous Fuel Safety Assessment for Light-Duty Automobile Vehicles*, prepared for U.S. DOE by Los Alamos National Laboratory, Report No. LA 9829-MS (Nov. 1983).

Lipari, F., et al., *Aldehyde and Unburned Fuel Emissions from Methanol-Fueled Heavy-Duty Diesel Engines*, SAE Paper 860307, International Congress and Exposition, Detroit (Feb. 24-28, 1986).

Machiele, P.A., *Flammability and Toxicity Tradeoffs with Methanol Fuels*, presented at International Fuels and Lubricants Meeting and Exposition, Toronto, SAE Paper 872064 (Nov. 1987).

McCabe, R.W., et al., *Catalyst Evaluations on a Detroit Diesel Allison 6V-92TA Methanol-Fueled Engine*, presented at International Fuels and Lubricants Meeting and Exposition, Toronto, SAE Paper No. 872138 (Nov. 1987).

Moses, D., and C. Saricks, *A Review of Methanol Vehicles and Air Quality Impacts*, presented at International Fuels and Lubricants Meeting and Exposition, Toronto, SAE Paper No. 872053 (Nov. 1987).

Mueller Associates, Inc., and E:F Technology, *Technology and Market Assessment of Gas-Fueled Vehicles in New York State*, prepared by Mueller Associates, Inc., and E:F Technology, Inc., for the New York State Energy Research and Development Authority and New York Gas Group, NYSEDA Report 83-15 (Aug. 1983).

Mueller Associates, Inc., *Gasoline Octane Enhancement: Technology, Economics, and Environmental, Health, and Safety Considerations*, prepared for U.S. Dept. of Energy Report DOE/PE/72013-1 (July 1985).

Mueller Associates, Inc., Baltimore, MD, unpublished information (Oct. 1987).

National Fire Protection Association., *Fire Protection Handbook*, 13th Ed., Quincy, Mass. (1977).

National Fire Protection Association, *NFPA Compressed Natural Gas (CNG) Vehicular Fuel Systems 1984*, Quincy, Mass. (1984).

Nichols, R., *A View of Flexible Fuel Vehicle Aldehyde Emissions*, SAE Paper No. 881200 (1988).

Nichols, R.J., *Update on Ford's Methanol Vehicle Experience*, presented at the European Fuel Oxygenates Association' 1st Annual Conference, Brussels (April 15, 1986).

Nichols, R.J., *Field Experience with U.S. Methanol Vehicles: Future Design Considerations*, presented at the Coordinating European Council's 2nd International Symp. on Performance and Evaluation of Automotive Fuels and Lubricants, Wolfsburg, W. Germany (June 5-7, 1985).

NOAA, *Chemical and Physical Properties of Refined Petroleum Products*, National Oceanic and Atmospheric Administration, U.S. Government Printing Office, Washington, D.C. (Oct. 1977).

Obert, E.F., *Internal Combustion Engines*, International Textbook Co., Scranton, Penn. (1968).

Perry, J.H., et al., *Chemical Engineer's Handbook*, 6th Ed., McGraw-Hill, New York (1977).

Potts, A.M., *The Basic Science of Poisons*, in Casarett and Doull's Toxicology, C.D. Klassen et al., eds., Macmillan, New York (1986).

Powrie, D., *Ford NGV Ranger Demonstration* (status report), Consumers' Gas Company Ltd. (March 1985)

Russell, A., and J. Harris, *A Quantitative Estimate of the Air Quality Effects of Methanol Fuel Use*, SAE Paper No. 881687, International Fuels and Lubricants Meeting and Exposition, Portland, Ore. (Oct 10-13, 1988).

Sapre, A., *Properties, Performance and Emissions Medium Concentration, Methanol-Gasoline Blends in a Single-Cylinder Spark Ignition Engine*, SAE Paper No. 881679 (1988).

Schiller, R., Ford Motor Co., private communication (March 1989).

Scott, C.B., *Alcohol Fuels—Summary of Key Information*, Unocal Corp., Los Angeles (May 1987).

Seisler, J., American Gas Association, Arlington, Va., unpublished information (Feb. 14, 1985).

Sharma, R.K., et al., *Ecological and Biomedical Effects of Effluents from Near-Term Electric Vehicle Storage Battery Cycles*, Argonne National Laboratory Report ANL/ES-90 (1980).

Shelton, E.M., *Diesel Fuel Oils, 1979*, Bartlesville Energy Technology Report No. BETC/PPS-79/5, for U.S. Dept. of Energy, Bartlesville, Okla. (1979).

Sierra Research, Inc., *Potential Emissions and Air Quality Effects of Alternate Fuels-Final Report*, Report No. SR89-03-04, Sacramento, Calif. (March 28, 1989).

Singh, M.K., *State of Knowledge of Environmental Concerns Related to Natural Gas-Fueled Vehicles*, Argonne National Laboratory Report ANL/CNSV-TM-138 (April 1984).

Singh, M.K., and R.R. Sekar, *Emission Reduction Effects of Methanol Vehicles: State of Knowledge*, Argonne National Laboratory Report ANL/EES-TM-352 (July 1988).

SMFTC, *Environmental Risks When Handling Alternate Fuels* (in Swedish), Swedish Motor Fuel Technology Co., prepared for the National Swedish Board for Energy Source Development (1983).

SMFTC, *Production, Handling, and Use of Alternate Motor Fuels in Western Europe* (in Swedish), Swedish Motor Fuel Technology Co., prepared for the Swedish Board for Technical Development and the Swedish Board for Energy Source Development, NE 1982:17, Stockholm (1982).

SMFTC, *Alcohols and Alcohol Blends as Motor Fuels, Volume IIA and IIB*, Swedish Motor Fuel Technology Co., International Energy Information, No. 580-1986 (Oct. 1986).

Sperling, D., *New Transportation Fuels: A Strategic Approach to Technological Change*, University of California Press, Berkeley (1988).

Sunshine, I., ed., *Handbook of Analytical Toxicology*, CRC Press (1975).

Wimer, W.W., et al., *Alcohols Toxicology*, presented at the International Energy Agency's 6th International Symposium on Alcohol Fuels Technology, Ottawa, Canada (May 21-25, 1984).